

Final

**Water Quality Analyses for Lead in the Inner Harbor/Northwest Branch and
Zinc in the Inner Harbor/Northwest Branch and Bear Creek Portions of
Baltimore Harbor in Baltimore City and Baltimore County, Maryland**

Prepared by:

Maryland Department of the Environment
Montgomery Park Business Center
1800 Washington Boulevard, Suite 540
Baltimore MD 21230-1718

Submitted to:

Watershed Protection Division
U.S. Environmental Protection Agency, Region III
1650 Arch Street
Philadelphia, PA 19103-2029

September 2004

Submittal Date: September 22, 2004
Approval Date: January 18, 2005

Table of Contents

List of Figures..... i

List of Tables i

List of Abbreviations ii

List of Abbreviations ii

EXECUTIVE SUMMARY iii

1.0 INTRODUCTION..... 1

2.0 GENERAL SETTING 3

3.0 WATER QUALITY CHARACTERIZATION..... 7

3.1 WATER COLUMN EVALUATION 9

3.2 SEDIMENT CHEMISTRY EVALUATION 11

3.3 SEDIMENT TOXICITY EVALUATION 12

4.0 CONCLUSION 14

5.0 REFERENCES..... 15

List of Figures

Figure 1: Watershed Map of the Baltimore Harbor..... 4
Figure 2: Land Use Map of the Inner Harbor/Northwest Branch Watershed 5
Figure 3: Land Use Map of the Bear Creek Watershed..... 6
Figure 4: Northwest Branch/Inner Harbor and Bear Creek Sampling Locations..... 8

List of Tables

Table 1: Land Use Composition of the Inner Harbor/Northwest Branch and Bear Creek.. 3
Table 2: Water Quality Analysis Stations for the Inner Harbor/Northwest Branch 9
Table 3: Water Quality Analysis Stations for Bear Creek..... 9
Table 4: Zinc and Pb Analysis Detection Limits..... 10
**Table 5: Inner Harbor/Northwest Branch Dissolved Zn and Pb
Water Column and Porewater Data..... 10**
Table 6: Bear Creek Dissolved Zn Water Column and Porewater Data..... 10
Table 7: Inner Harbor/Northwest Branch Sediment Data 11
Table 8: Inner Harbor/Northwest Branch Sediment Data 11
Table 9: Bear Creek Sediment Data..... 12
Table 10: Inner Harbor/Northwest Branch Sediment Toxicity Data 13
Table 11: Bear Creek Sediment Toxicity Data..... 13

List of Abbreviations

ANOVA	Analysis of Variance
AVS	Acid Volatile Sulfides
AVS-SEM	Acid Volatile Sulfides – Simultaneously Extracted Metals
BSM	Baltimore Sediment Mapping Study
CBL	Chesapeake Biological Laboratory
COMAR	Code of Maryland Regulations
Cr	Chromium
CWA	Clean Water Act
EPA	Environmental Protection Agency
ERM	Effects Range Median
ERM-Q	Effects Range Median Quotient
MDE	Maryland Department of the Environment
MDP	Maryland Department of Planning
mg/kg DW	Milligram/kilogram Dry Weight Basis
Pb	Lead
PCB	Polychlorinated Biphenyls
TMDL	Total Maximum Daily Load
µg/L	Micrograms per Liter
µmole/g	Micromoles per gram
WQA	Water Quality Analysis
WQLS	Water Quality Limited Segment
Zn	Zinc

Final

EXECUTIVE SUMMARY

Section 303(d) of the federal Clean Water Act (CWA) and the U.S. Environmental Protection Agency (EPA)'s 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, the State is 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 that water quality standards are being met.

The Baltimore Harbor, with its watershed located in Baltimore City and parts of Baltimore, Howard, Anne Arundel, and Carroll Counties was identified on the 1996 303(d) list as impaired by toxic substances, nutrients, and suspended sediments. In 1998, the impairment listings were refined to include specific impairing substances and increased spatial resolution based on an analysis of bulk sediment contaminant concentrations compared to non-regulatory screening values. As a result, the Inner Harbor/Northwest Branch (basin code 02-13-09-03) was listed for fecal coliform, chromium (Cr), zinc (Zn), lead (Pb), and polychlorinated biphenyls (PCBs). In 2002 it was listed for biological community impacts. Bear Creek, a tributary to Baltimore Harbor (basin code 02-13-09-03) located in Baltimore County, was included in the 1996 303(d) listing for the Baltimore Harbor. However, in 1998 the increased spatial resolution led to Bear Creek being identified as impaired specifically for the substances Cr, Zn, and PCBs.

This report provides analyses of the data used to determine the Inner Harbor/Northwest Branch and Bear Creek Zn impairment listings and Inner Harbor/Northwest Branch Pb impairment listing. It also includes recently collected data that indicates that although sediment toxicity is present in the Inner Harbor/Northwest Branch and Bear Creek, the source of the toxicity cannot be attributed to Zn and Pb. As a result, the analyses support the conclusion that TMDLs for Zn and Pb are not currently necessary. However, the segments will remain listed as impaired for biological community impacts due to sediment toxicity pending a field study scheduled to begin in September 2004 and be completed by December 2005. The goal of the study is to identify the substance or substances that are causing the sediment toxicity observed in these segments and to address the potential that sediment ingestion could be a route of exposure not fully accounted for by these procedures.

Barring the receipt of any contradictory data, this report will be used to support the removal of Zn and Pb as impairing substances in the Inner Harbor/Northwest Branch and Bear Creek on Maryland's list of WQLSs when the Maryland Department of the Environment (MDE) proposes the revision of Maryland's 303(d) list for public review in the future. The nutrients and Cr impairments are currently being addressed under separate analyses; the suspended sediments, biological community, fecal coliform, and PCB impairments will be addressed at a future date.

Although the waters of the Inner Harbor/Northwest Branch and Bear Creek do not currently display signs of toxicity due to Zn and Pb, the State reserves the right to reassess the impact(s) of Zn and Pb on the environment due to future changes in Baltimore Harbor water quality, including, but not limited to the improvement of dissolved oxygen levels due to a reduction in

Final

nutrients. Furthermore, the State reserves the right to require additional pollutant controls in the Inner Harbor/Northwest Branch and Bear Creek if evidence suggests that Zn or Pb from either basin is contributing to water quality problems within Baltimore Harbor.

Final

1.0 INTRODUCTION

Section 303(d) of the federal Clean Water Act (CWA) and U.S. 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. This list of impaired waters is commonly referred to as the "303(d) list". For each WQLS, the State is to either establish a Total Maximum Daily Load (TMDL) of the specified substance that the waterbody can receive without violating water quality standards, or demonstrate that water quality standards are being met.

A segment identified as a WQLS may not require the development and implementation of a TMDL if current information contradicts the previous finding of an impairment. The most common factual scenarios obviating the need for a TMDL are as follows: 1) more recent data indicating that the impairment no longer exists (i.e., water quality criteria are being met); 2) more recent and updated water quality modeling demonstrates that the segment is now attaining the criteria; 3) refinements to water quality criteria, or the interpretation of those standards, which result in criteria being met; or 4) correction to errors made in the initial listing.

The Baltimore Harbor, with its watershed located in Baltimore City and parts of Baltimore, Howard, Anne Arundel, and Carroll Counties was identified on the 1996 303(d) list as impaired by toxic substances, nutrients, and suspended sediments. In 1998, the impairment listings were refined to include specific impairing substances and increased spatial resolution. As a result, the Inner Harbor/Northwest Branch (basin code 02-13-09-03) was listed for fecal coliform, chromium (Cr), zinc (Zn), lead (Pb), and polychlorinated biphenyls (PCBs). In 2002 it was listed for biological community impacts. Bear Creek, a tributary to Baltimore Harbor, (basin code 02-13-09-03) located in Baltimore County, was included in the 1996 303(d) listing for the Baltimore Harbor. However, in 1998 the increased spatial resolution led to Bear Creek being identified as impaired specifically for the substances Cr, Zn, and PCBs.

The 1998 impairment listings for Zn and Pb were based on the bulk sediment concentrations of Zn and Pb, acute sediment toxicity, and benthic integrity data generated during the Baltimore Harbor Sediment Mapping Study (BSM). The data collected during the BSM revealed high levels of toxic metals (including Zn and Pb), and organic compounds in both the Inner Harbor/Northwest Branch and Bear Creek. Additionally, the BSM toxicity test results indicated elevated levels of toxicity associated with the sediments in these regions. Since toxicity to aquatic life (*Leptocheirus plumulosus*) was evident, and no water quality criteria for toxic contaminants in sediment were available, the sediment concentrations were evaluated against the Effects Range Median (ERM) concentration; a commonly used sediment quality benchmark (Long *et al.*, 1995; MacDonald *et al.*, 1996). The ERM guidelines are based on data from 89 reports that contain simultaneous measures of sediment toxicity and chemistry. The ERM designates the sediment contaminant level at which half [50th percentile] of the studies reported harmful effects. As a result of these analyses, the Maryland Department of the Environment (MDE) concluded that Zn in the Inner Harbor/Northwest Branch and Bear Creek and Pb in the

Final

Inner Harbor/Northwest Branch were to be considered impairing substances due to the frequency and magnitude of the exceedance of the ERM, as well as the observed sediment toxicity.

However, during discussions with the Baltimore Harbor TMDL Stakeholder Advisory Group stakeholders raised questions regarding the MDE's water quality endpoints. The questions were focused on the appropriateness of an ERM based endpoint because ERM values are screening values and the authors of the ERM endpoints explicitly warned that they should not be used for regulatory purposes. The justification for the development of this endpoint was the lack of EPA promulgated water quality criteria for toxics present in sediment. The MDE's endpoints were based on sediment concentrations of Zn and Pb; the endpoint for each constituent was set at an ERM-Quotient (ERM-Q) value of 0.5. The ERM-Q is an evaluation method used to develop a spatial average of a specific contaminant within a given region based on several sample sites and data points (MDE, 2002).

Based on the issues raised by stakeholders, the initial listings for Zn and Pb were brought into question because; 1) the original listings were based on Zn and Pb sediment concentrations evaluated against the ERM guideline value, 2) the current aquatic life water quality criteria for Zn and Pb are based on dissolved water column concentrations, and 3) the ERMs do not account for mitigating factors such as acid volatile sulfides (AVS) that precipitates metals into compounds that render them biologically unavailable. AVS is very high in Inner Harbor/Northwest Branch and Bear Creek sediments.

The water quality analyses (WQA) for Zn in the Inner Harbor/Northwest Branch and Bear Creek and Pb in the Inner Harbor/Northwest Branch was conducted using more recent water column, porewater, and sediment concentration data. The data collected includes dissolved Zn and Pb concentrations in the water column and porewater matrices. The results indicate that the porewater concentrations of Zn do not exceed the water column saltwater aquatic life criterion (chronic) of 81µg/L in Bear Creek and the water column freshwater aquatic life criterion (chronic) of 120µg/L in the Inner Harbor/Northwest Branch (Code of Maryland Regulations (COMAR) 26.08.02.03-2G) (See Table 5 and 6). The results also indicate that porewater concentrations of Pb do not exceed the water column chronic freshwater aquatic life criterion of 2.5µg/L in the Inner Harbor/Northwest Branch (COMAR 26.08.02.03-2G) (See Table 5). The nutrients and Cr impairments are currently being addressed under separate analyses whereas, the suspended sediments, biological community, fecal coliform, and PCB impairments will be addressed at a future date.

Barring contradictory data, this report will be used to support the removal of Zn as an impairing substance in the Inner Harbor/Northwest Branch and Bear Creek and Pb as an impairing substance in the Inner Harbor/Northwest Branch on Maryland's list of WQLSs when MDE proposes the revision of Maryland's 303(d) list for public review in the future. However, the segments will remain listed as impaired for biological community impacts due to sediment toxicity. In addition, MDE is funding a "stressor identification" study to determine which substances, including some not previously analyzed, may be causing the sediment toxicity. The remainder of this report presents the general setting of the waterbody and presents a discussion and conclusions relative to the water quality characterization process.

Final

2.0 GENERAL SETTING

The Inner Harbor/Northwest Branch and the Bear Creek watersheds are located in the Patapsco/Back River region of the Chesapeake Bay watershed within Maryland (see Figure 1). The Inner Harbor/Northwest Branch watershed is within Baltimore City and has a drainage area of 42,000 acres consisting of the Jones Falls watershed and two subwatersheds that drain directly into the Inner Harbor/Northwest Branch. The land use profile in this watershed include forest and other herbaceous (6,648 acres or 16%), mixed agriculture (3,400 acres or 8%), and urban (31,561 acres or 76%). The water surface area is 164 acres (<1%). Table 1 highlights the land use within the Inner Harbor/Northwest Branch watershed.

Bear Creek, located within Baltimore County, is a highly urbanized tidal creek in the Baltimore Harbor watershed that drains an area of approximately 5,900 acres. The land use in this watershed consists of forest and other vegetation (400 acres or 7%), and urban (5,300 acres or 91%). The water surface area is 100 acres (2%). Table 1 highlights the land use within the Bear Creek watershed.

Table 1: Land Use Composition of the Inner Harbor/Northwest Branch and Bear Creek

Region	Forest/Herbaceous	Mixed Agriculture	Urban	Water
Inner Harbor/Northwest Branch	16%	8%	76%	<1%
Bear Creek	7%	0%	91%	2%

The Baltimore Harbor watershed, including the Inner Harbor/Northwest Branch and Bear Creek, lies within the Piedmont and Coastal Plain of Central Maryland. The surficial rocks of the Piedmont have formed from the decomposition of various sedimentary, metamorphic, and igneous parent materials. Underlying parent material consists of schist, limestone, marble and gneiss. Exposed igneous rocks such as gneiss and Baltimore gabbro typify the stream valleys along the fall line between the Piedmont and Coastal Plain. These formations are resistant to short-term erosion and often determine the limits of stream bank and streambed. These crystalline formations decrease in elevation from northwest to southeast and eventually extend beneath the younger sediments of the Coastal Plain. The fall line represents the transition between the Coastal Plain and the Piedmont. The Coastal Plain surficial geology is characterized by unconsolidated marine and riverine sediments deposited over the crystalline rock of the piedmont (Coastal Environmental Services, 1995).

A summary of land use for the Inner Harbor/Northwest Branch and Bear Creek watersheds are given in Figures 2 and 3, respectively. Based on the 1997 land use assessment developed by the Maryland Department of Planning (MDP), MDE aggregated the 22 land uses identified in the Baltimore Harbor watershed down to 10 land uses for modeling purposes. Using these 10 land use categories MDE classified the land uses Commercial/Industrial, High, Medium and Low Density Residential as urban land uses. These urban categories represent 76 % of the Inner Harbor/Northwest Branch and 91% of the Bear Creek watershed, respectively.

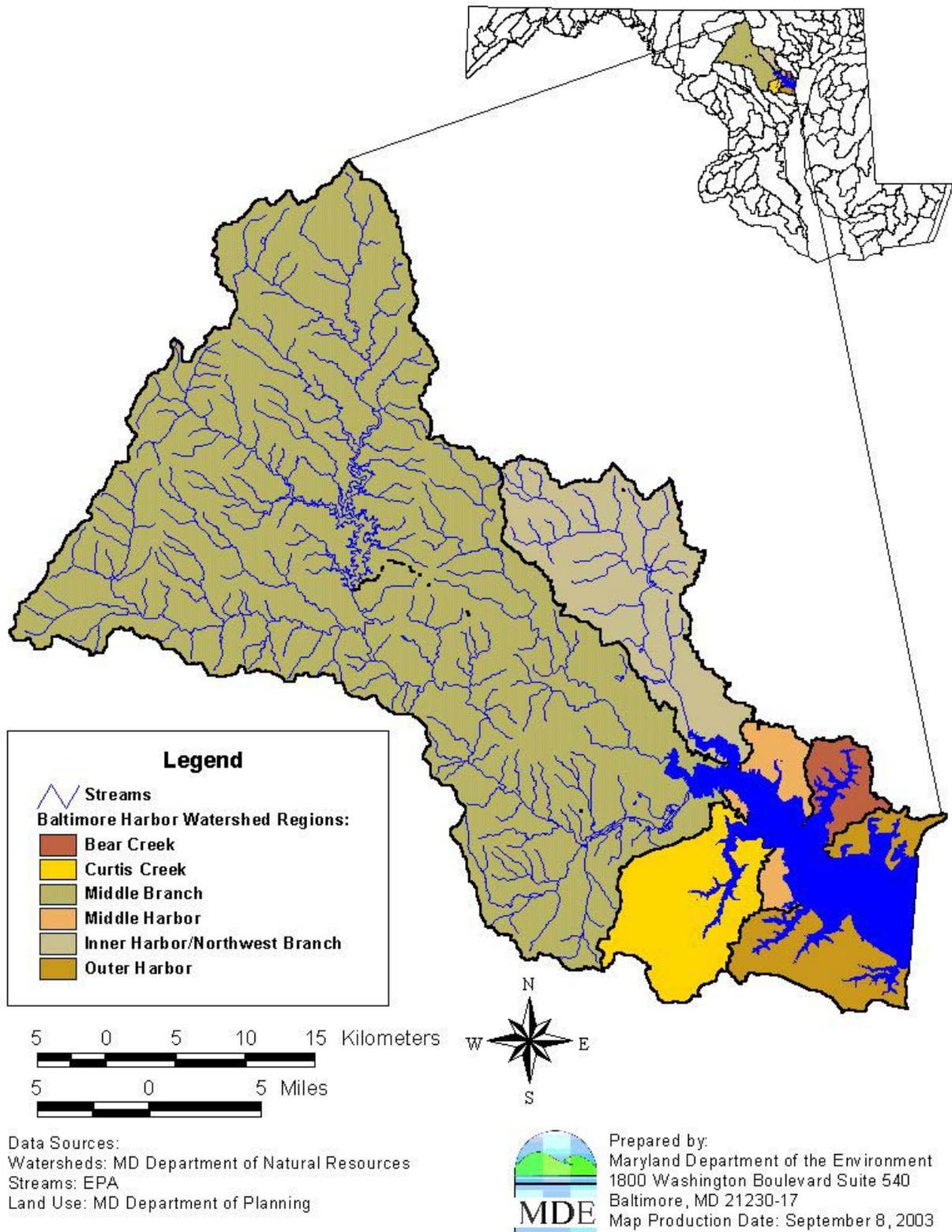


Figure 1: Watershed Map of the Baltimore Harbor

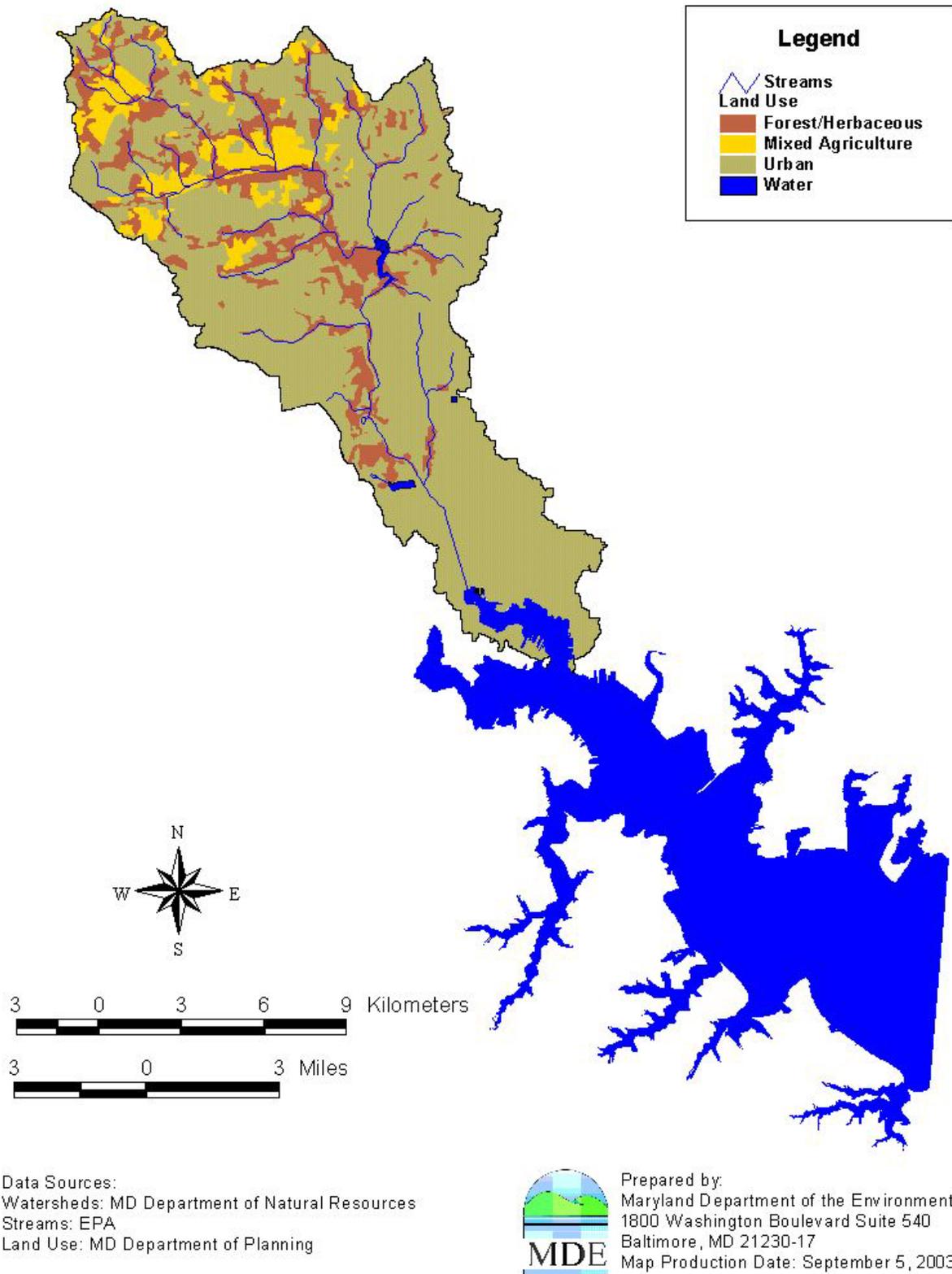


Figure 2: Land Use Map of the Inner Harbor/Northwest Branch Watershed

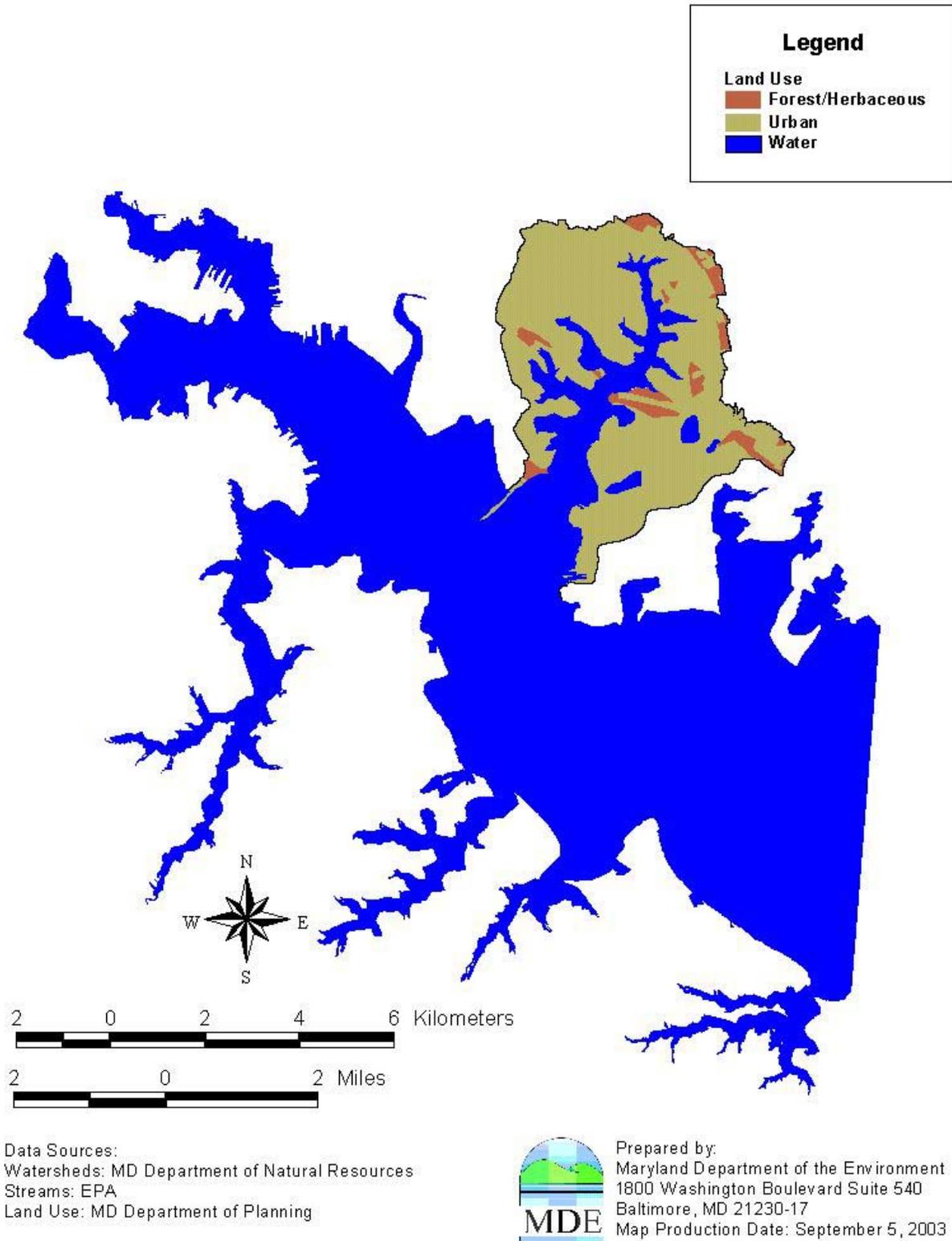


Figure 3: Land Use Map of the Bear Creek Watershed

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. The criteria developed to protect the designated use may differ and are dependent upon the specific designated use(s) of a waterbody.

Maryland's water quality standards presently include numeric criteria for Zn and Pb in the water column based on the need to protect aquatic life, wildlife and human health. An interpretation of the narrative water quality standards exists for toxic substances to address sediment quality and ensure the surficial bottom sediments of a waterbody are capable of supporting aquatic life, thus protecting the designated uses.

The Maryland Surface Water Use Designation COMAR 26.08.02.08J for the Baltimore Harbor and its tributaries (including the Inner Harbor/Northwest Branch and Bear Creek) is Use I – water contact recreation, fishing, and protection of aquatic life and wildlife. The applicable numeric water quality criteria, based on chronic toxicity, for Zn is 81µg/L in saltwater and 120µg/L in freshwater. The applicable numeric water quality criteria, based on chronic toxicity, for Pb is 2.5µg/L in freshwater (COMAR 26.08.02.03-2G). The Inner Harbor/Northwest Branch segment is defined in COMAR 26.08.02.03-1B as freshwater. To assess if the segments are impaired the porewater data will be evaluated against the water column water quality criterion.

A water column and sediment survey was conducted at stations 68, 69, 70, 71, and 73 in the Inner Harbor/Northwest Branch and stations 28, 29, 30, 31, 32 in Bear Creek in August 2003 (see Figure 4 and Tables 2 and 3). The data from this sampling effort will support this WQA. For each sample, concentrations were determined for: 1) dissolved Zn and Pb in the water column (1 meter from the bottom); 2) dissolved Zn and Pb in the surficial sediment porewater; 3) Zn and Pb chemistry, acid volatile sulfide – simultaneously extracted metals (AVS-SEM), and sulfides in surficial (< 2cm in depth) sediment; and 4) chronic toxicity bioassays (28-day *L. plumulosus*) on surficial sediment. The water column and surficial sediment porewater data presented in Section 3.1, Table 5 and Table 6, indicates that concentrations of Zn and Pb do not exceed quality criteria in either the water column or the surficial sediment porewater.

The sediment data is presented in Section 3.2, Tables 7 – 9, indicate that high sediment concentrations of Zn and Pb remain present in the surface sediments. However, utilized a molar-based analysis of the metals to account for the varying molecular weights of the compounds, the data indicates that the amount of sulfides present in the sediments is well above the amount necessary to reduce all divalent metals, including the Zn and Pb, into metallic sulfide compounds that render them non-bioavailable.

The ambient sediment bioassay data is presented in Section 3.3, Tables 10 and 11, indicate that toxicity occurs at 9 of the 10 Inner Harbor/Northwest Branch and Bear Creek stations sampled (Fisher, 2004). However, due to the presence of many contaminants at elevated levels in the sediment and porewater concentrations of Zn and Pb that do not exceed the applicable water quality standard, MDE is unable to assign the cause of toxicity to either metal.

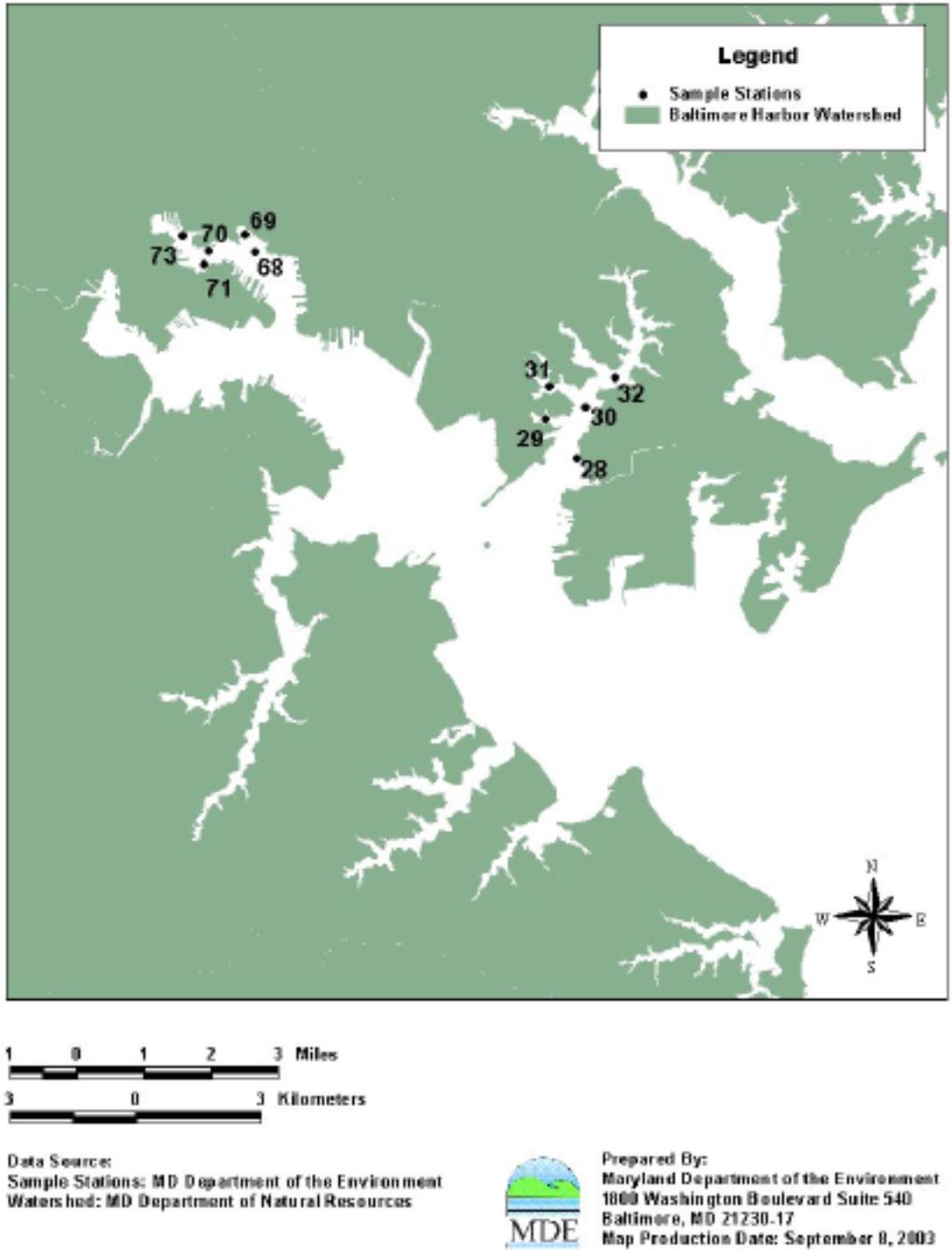


Figure 4: Northwest Branch/Inner Harbor and Bear Creek Sampling Locations

3.1 WATER COLUMN EVALUATION

To evaluate the water quality of the Inner Harbor/Northwest Branch and Bear Creek, MDE evaluated the porewater concentrations of Zn and Pb against the aquatic life chronic criteria for each contaminant in the water column. The samples collected for these analyses were taken from stations established during the 1996 BSM. Table 2 and Table 3 contain the station identifications, geographical coordinates, and descriptive locations of the stations in the Inner Harbor/Northwest Branch and Bear Creek, respectively.

Table 2: Water Quality Analysis Stations for the Inner Harbor/Northwest Branch

Station ID	GPS Coordinates	Station Description
BSM 68	39.278 76.583	Southeast of Fells Pt.
BSM 69	39.282 76.586	Southeast of Fells Pt.
BSM 70	39.278 76.596	South of former chromium refinery
BSM 71	39.275 76.598	Across channel from former chromium refinery
BSM73	39.283 76.609	Head of Inner Harbor

Table 3: Water Quality Analysis Stations for Bear Creek

Station ID	GPS Coordinates	Station Description
BSM 28	39.233 76.495	Mouth of Bear Creek near International Steel
BSM 29	39.242 76.503	Cove Northwest of Route 695 bridge
BSM 30	39.244 76.492	Mid Creek adjacent to railroad bridge
BSM 31	39.248 76.502	Head of small tributary entering Creek at railroad bridge
BSM32	39.250 76.484	Head of Bear Creek/South of Wise Ave. bridge

Water column and porewater samples were collected in August 2003 by the University of Maryland, Chesapeake Biological Laboratory (CBL) and shipped to Frontier Geosciences in Seattle, WA for extraction and analysis. The porewater was separated from the surficial sediments by centrifugation, filtered to remove particulate matter and analyzed. The filtrate was analyzed for Zn and Pb in the dissolved phase using a standard metals analysis. The values were assessed against the water quality criteria to determine if a violation of the water quality standard

Final

occurred. The Zn and Pb data from the water column and porewater analysis are presented in Table 5 and Table 6. The detection limits for the Zn and Pb analysis are displayed in Table 4.

Table 4: Zinc and Pb Analysis Detection Limits

Analyte	Detection Limit
Zn Water Column	0.08 µg/L
Zn Sediment	1.0 mg/kg
Pb Water Column	0.05 µg/L
Pb Sediment	0.30 mg/kg

Table 5: Inner Harbor/Northwest Branch Dissolved Zn and Pb Water Column and Porewater Data

Station	Water Column		Porewater	
	Zn	Pb	Zn	Pb
	µg/L		µg/L	
BSM68	20.8	0.05	1.9	0.80
BSM69	24.0	0.13	4.9	1.18
BSM70	23.6	<0.05	2.1	1.58
BSM71	29.7	0.11	1.9	1.47
BSM73	20.0	<0.05	3.7	0.99

Chronic water quality criteria for freshwater for Zn is = 120µg/L and Pb is 2.5µg/L

Table 6: Bear Creek Dissolved Zn Water Column and Porewater Data

Station	Water Column	Porewater
	Zn	
	µg/L	
BSM28	2.25	1.77
BSM29	5.89	1.20*
BSM30	11.90	1.56
BSM31	8.63	1.54
BSM32	8.69*	1.10

Chronic water quality criteria for saltwater for Zn is = 81µg/L

*Value is average of duplicate samples

3.2 SEDIMENT CHEMISTRY EVALUATION

To evaluate the sediment conditions, bulk surficial (top 2 cm) sediment samples were collected by CBL in the Inner Harbor/Northwest Branch and Bear Creek using a petite ponar dredge. The sediment stations correspond to the monitoring stations sampled in the BSM and the water column survey described in the above sections. Refer to Table 1 and Table 2 for station locations. The samples collected were analyzed for Zn and Pb, AVS/SEM, and sulfides. The results of the analysis are presented in Tables 7, 8, and 9.

Table 7: Inner Harbor/Northwest Branch Sediment Data*

Station	Total Zn	AVS/SEM Zn	AVS/SEM Divalent Metals Cu, Cd, Zn, Pb	AVS	Excess Sulfides
	mg/kg DW**	μmole/g	μmole/g	μmole/g	μmole/g
BSM68	661	6.41	7.46	78.75	71.29
BSM69	704	6.64	7.91	359.38	351.47
BSM70	790	6.46	7.59	173.44	165.85
BSM71	970	9.10	10.78	196.88	186.10
BSM73	618	5.95	7.13	236.25	229.12

*The analysis is presented on a molar basis to account for the various molecular weights of the analytes.

**DW = Dry Weight

Table 8: Inner Harbor/Northwest Branch Sediment Data*

Station	Total Pb	AVS/SEM Pb	AVS/SEM Divalent Metals Cu, Cd, Zn, Pb	AVS	Excess Sulfides
	mg/kg DW**	μmole/g	μmole/g	μmole/g	μmole/g
BSM68	298	1.01	7.46	78.75	71.29
BSM69	352	1.22	7.91	359.38	351.47
BSM70	394	1.10	7.59	173.44	165.85
BSM71	470	1.63	10.78	196.88	186.10
BSM73	312	1.14	7.13	236.25	229.12

*The analysis is presented on a molar basis to account for the various molecular weights of the analytes.

**DW = Dry Weight

Table 9: Bear Creek Sediment Data*

Station	Zn	AVS/SEM Zn	AVS/SEM Divalent Metals Cu, Cd, Zn, Pb	AVS	Excess Sulfides
	mg/kg DW**	μmole/g	μmole/g	μmole/g	μmole/g
BSM28	1,530	17.13	19.42	144.06	124.64
BSM29***	1,930	16.16	21.29	304.06	282.77
BSM30	1,870	27.82	31.58	340.63	309.05
BSM31	2,230	17.89	19.14	500.00	480.86
BSM32	1,490	17.74	19.78	375.00	355.22

*The analysis is presented on a molar basis to account for the various molecular weights of the analytes.

**DW = Dry Weight

***Results are an average of duplicate samples

Baltimore Harbor sediments are acted upon by chemical reactions that result in the Zn and Pb being sequestered into non-reactive forms. In the low dissolved oxygen environment found in the Harbor high levels of sulfides have accumulated in the sediments. Recent EPA studies indicate that sulfide compound reactions dominate the sediment chemistry reactions of cationic metals such as Zn and Pb (Boothman et. al., 2000 and Berry et. al., 2002). Based on this information, the data presented in Tables 7-9 were assessed using a molar analysis to determine the molecular balance of compounds found within the sediments. The data presented indicate that the levels of AVS present within the sediment are well above those needed to fully react with Zn, Pb, and other divalent metals. As a result, the high concentrations of total Zn and Pb found within the sediments do not correspond to the reactive amounts available to partition to the water column or that may be biologically available.

3.3 SEDIMENT TOXICITY EVALUATION

To complete the WQA, sediment quality in the Inner Harbor/Northwest Branch and Bear Creek was evaluated using a 28-day chronic growth and survival whole sediment test with the marine amphipod *L. plumulosus*. This species was chosen because of its ecological relevance to the waterbody of concern. *L. plumulosus* is an EPA-recommended test species for assessing the toxicity of estuarine or marine sediments (EPA, 2001). Surficial (top 2 cm) sediment samples were collected by CBL in the Inner Harbor/Northwest Branch and Bear Creek using a petite ponar dredge. The sediment stations correspond to the monitoring stations sampled in the BSM and the water column survey described in the above sections. Refer to Table 1 and Table 2 for station locations. Sediment toxicity test results are presented in Table 10 and Table 11.

Table 10: Inner Harbor/Northwest Branch Sediment Toxicity Data

Station	Percent	Growth	Reproduction
	Survival	mg/ind/d ¹	Neonates/Individual
Control	88	0.065	4.94
BSM68*	61	0.039	0.47
BSM69*	35	0.044	0.18
BSM70*	9.4	0.032	0.00
BSM71*	3	0.021	0.30
BSM73*	55	0.054	0.94

¹Growth rate equals milligram/individual/day

*Significant observed toxicity

Table 11: Bear Creek Sediment Toxicity Data

Station	Percent	Growth	Reproduction
	Survival	mg/ind/d ¹	Neonates/Individual
Control	87	0.068	4.34
BSM28*	0	0	0.00
BSM29*	72	0.063	3.26
BSM30*	2	0.014	0.00
BSM31	80	0.049	1.45
BSM32*	61	0.050	1.90

¹Growth rate equals milligram/individual/day

*Significant observed toxicity

The endpoints for the 28-day test were survival, growth rate (mg dry weight/individual/day) and reproduction (neonates/survivor). Data were analyzed in accordance with procedures outlined in the EPA 2001 method (EPA, 2001). Survival data were arcsine square-root transformed prior to analysis. The survival data were then assessed for normality and homogeneity of variance using the Chi-Square Test and Bartlett's Test, respectively ($\alpha = 0.05$). All transformed survival data were normal and homogeneous. The survival data were then analyzed via Analysis of Variance (ANOVA) followed by comparisons between test sediment amphipod survival and the control amphipod survival using a Dunnett's Test ($\alpha = 0.05$).

All of the sediments from the sites tested showed significant reductions in test endpoints. BSM sites 28, 29, 30, 32, 68, 69, 70, 71, and 73 showed reduced survival of *L. plumulosus* (Tables 10 and 11). The most significant effects were seen at BSM 28 (0% survival), BSM 30 (2% survival), BSM 70 (9.4% survival), and BSM 71 (3.0% survival). Statistical analyses of sublethal endpoints were conducted only on treatments not exhibiting significant effects on survival after 28 days. Since only one site, BSM 31, did not have a reduction in survival, a two-sample t-Test ($\alpha = 0.05$) was used to compare growth rate and reproduction at BSM 31 with the control endpoints for that suite of sample sites. Although there was not a reduction in growth

Final

rate at this site, amphipods from this station showed a significant reduction in reproduction (1.45 neonates per survivor versus 4.34 neonates per survivor in the control).

4.0 CONCLUSION

The data presented in support of the WQA indicate that porewater and water column concentrations of Zn in the Inner Harbor/Northwest Branch and Bear Creek, and Pb in the Inner Harbor/Northwest Branch do not exceed water quality standards. The toxicity data indicates mortality was found in the Inner Harbor/Northwest Branch and Bear Creek sediments. However, sediment data collected for AVS/SEM metals plus sulfides indicate that in situ environmental conditions (i.e., low dissolved oxygen, high BOD) have produced high sulfide concentrations within the sediments. The sulfide levels are well in excess of what is needed to sequester Zn and Pb into metallic sulfide compounds that render them unavailable to partition into the porewater in quantities that violate water quality standards. This relationship indicates the probability that neither Zn nor Pb are bioavailable for sediment dwelling organisms and cannot be determined as the specific cause of the observed toxicity.

Therefore, barring any contradictory data, this information provides sufficient justification to remove Zn and Pb from Maryland's 303(d) list as impairing substances in the Inner Harbor/Northwest Branch and Bear Creek. The segments will continue to be listed for toxicity based on the data collected in the WQA effort. To address the sediment toxicity impairment, MDE is conducting a field study scheduled to begin in September 2004 and be completed by December 2005. The goal of the study is to identify the substance or substances that are causing the sediment toxicity observed in these segments and to address the potential that sediment ingestion could be a route of exposure not fully accounted for by these procedures. Information on the study can be attained from MDE upon request by contacting the TMDL outreach staff at 410-537-3902. Once the study is completed MDE will utilize the information to begin developing TMDLs for the compound or compounds identified as causes of toxicity.

Final

5.0 REFERENCES

- Berry, W.J. et al., Effects of Chromium in Sediment: 1 Toxicity Tests With Saltwater Field Sediments, USEPA, National Health and Environmental Effects Research Laboratory, Atlantic Ecology Division. Narragansett, RI. November 2002.
- Boothman W.S., et al., Predicting Toxicity of Chromium Spiked Sediments by using Acid Volatile Sulfide and Interstitial Water Measurements. USEPA, National Health and Environmental Effects Research Laboratory, Atlantic Ecology Division. Narragansett, RI. April 2000.
- COMAR 26.08.02.03-2G. Numerical Criteria for Toxic Substances in Surface Waters.
- COMAR 26.08.02.03-1B. Toxic Substance Water Quality Criteria for Surface Waters.
- COMAR 26.08.02.08J. Stream Segment Designations.
- Coastal Environmental Services., Patapsco/Back Rivers Watershed Study, September 1995.
- Fisher, D., et al., Chronic Toxicity on Sediment From the Inner Harbor and Bear Creek to *Leptocheirus plumulosus*. University of MD, Wye Research and Education Center, May 2003.
- Environmental Protection Agency. 2001. Methods for Assessing the Chronic Toxicity of Marine and Estuarine Sediment-associated Contaminants with the Amphipod *Leptocheirus plumulosus*. EPA/600/R-01/020. First Edition. Office of Research and Development, Washington, DC.
- Long ER, MacDonald DD, Smith SL, Calder FD. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ Manage* 19:81–97.
- MacDonald DD, Carr RS, Calder FD, Long ER. 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* 5:253–278.
- Maryland Department of Environment, 2002 List of Impaired Surface Waters [303(d) List] and Integrated Assessment of Water Quality in Maryland, Section 4.5.4.2, September 2002.
- Maryland Department of Planning, 1997 Land Use, Land Cover Map Series, 1997.