# Water Quality Analyses of Chromium in the Inner Harbor/Northwest Branch and Bear Creek Portions of Baltimore Harbor in Baltimore City and Baltimore County, Maryland

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#### List of Abbreviations

ANOVA Analysis of Variance

AVS-SEM Acid Volatile Sulfide – Simultaneously Extracted Metals

BOD Biological Oxygen Demand

BSM Baltimore Harbor Sediment Mapping Study

CBL Chesapeake Biological Laboratory

Cd Cadmium cm Centimeter

COMAR Code of Maryland Regulations

Cr Chromium

Cr III Trivalent Chromium
Cr VI Hexavalent Chromium

Cu Copper

CWA Clean Water Act

EPA Environmental Protection Agency

ERM Effects Range Median

ERM-Q Effects Range Median Quotient

ICP-MS Inductively Coupled Plasma – Mass Spectrometry

MDE Maryland Department of the Environment

MDP Maryland Department of Planning

mg/Kg DW Milligram per Kilogram on a Dry Weight Basis

Pb Lead

PCBs Polychlorinated Biphenyls

ppm Parts per Million

TMDL Total Maximum Daily Load

μg/L Micrograms per Liter WQA Water Quality Analysis

WQLS Water Quality Limited Segment

Zn Zinc

#### **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. 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 Cr impairment listings. 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 Cr. As a result, the analyses support the conclusion that TMDLs for Cr are not currently necessary. However, the segments will remain listed as impaired for biological community impacts due to sediment toxicity.

Barring the receipt of any contradictory data, this report will be used to support the removal of total Cr as an impairing substance in the Inner Harbor/Northwest Branch and Bear Creek on Maryland's list of WQLSs when MDE proposes the revision of Maryland's 303(d) list for public review in the future. The nutrients, Zn, and Pb impairments are currently being addressed under separate analyses; the suspended sediments, biological, 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 Cr, the State reserves the right to reassess the impact(s) of all Cr species 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 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 Cr from either basin is contributing to water quality problems within Baltimore Harbor.

#### 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 currently 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 must 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 met.

A segment identified as a WQLS may not require the development 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 listings for Cr were based on the bulk sediment concentration of total Cr, 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 total Cr), 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 [50<sup>th</sup> percentile] of the studies reported harmful effects. As a result of these analyses, the Maryland Department of the Environment (MDE) concluded that total Cr in the Inner Harbor/Northwest Branch and Bear Creek was to be considered an impairing substance 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 justification of the Cr impairment and the MDE - developed water quality endpoint. The questions regarding the impairment listings focused on the use of total Cr sediment concentrations, given that Cr exists in two major valence states, trivalent (Cr III) or hexavalent (Cr VI), depending upon the presence of oxygen in the sediment and overlying water column. The distinction between the two major valence states is significant due to the toxicity associated with each species; Cr III is relatively non-toxic, and Cr VI is highly toxic. The current science indicates that reduction/oxidation conditions present within the water column and sediment govern the chemistry of Cr. Within Baltimore Harbor, the presence of low dissolved oxygen in the water column for significant time periods and high levels of biologically oxygen demanding (BOD) substances within the sediment facilitate the conversion of Cr VI to Cr III. Additionally, the relatively insoluble Cr III is also subject to reactions that create stable oxides and hydroxides that are unavailable for partitioning into porewater (Baker, Personnel Communication 2004).

The questions regarding the MDE - developed endpoint were focused on the appropriateness of the ERM - based endpoint because ERM values are screening values and the authors 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 toxic substances present in the sediment. The MDE - developed endpoint was based on sediment concentrations of total Cr 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 listing for Cr was brought into question because: 1) the original listing was based on the total Cr concentration in sediment evaluated against the ERM guideline value; 2) current aquatic life water quality criteria exist for Cr III and Cr VI in the dissolved state; and 3) water quality data evaluated did not contain data on Cr III and Cr VI.

The water quality analyses (WQA) for total Cr in the Inner Harbor/Northwest Branch and Bear Creek was conducted using recently collected water column, pore water, and sediment concentration data. The data collected includes Cr III and Cr VI for the water column and pore water matrices. The results indicate that the pore water concentrations of Cr VI do not exceed the water column saltwater aquatic life criterion (chronic) of  $50\mu g/L$  for Cr VI in Bear Creek and the water column fresh water aquatic life criterion (chronic) of  $11\mu g/L$  for Cr VI in the Inner Harbor/Northwest Branch (Code of Maryland Regulations (COMAR) 26.08.02.03-2G) and there is therefore is no basis for concluding that Cr is an impairing substance. The nutrients, Zn, and Pb impairments are currently being addressed under separate analyses whereas the suspended sediments, biological, and PCB impairments will be addressed at a future date.

Barring contradictory data, this report will be used to support the removal of total Cr as an impairing substance in the Inner Harbor/Northwest Branch and Bear Creek 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 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 lays out the general setting of the waterbody and presents a discussion and conclusions relative to the water quality characterization process.

## 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; the Bear Creek watershed is within Baltimore County. The Inner Harbor/Northwest Branch has a drainage area of 42,000 acres, which consists of the Jones Falls watershed and two subwatersheds that drain directly into the Inner Harbor/Northwest Branch. The land use profile in these areas include forest and other vegatation (6,648 acres or 16%), mixed agriculture (3,400 acres or 8%), and urban (31,561 acres or 76%). The water surface area of Inner Harbor/Northwest Branch is 164 acres (<1%). Table 1 shows the land use of the Inner Harbor/Northwest Branch watershed.

Bear Creek, a highly urbanized tidal creek in the Baltimore Harbor, drains a watershed area of approximately 5,900 acres. The land use in this watershed consists of forest and other herbaceous cover (400 acres or 7%), and urban (5300 acres or 91%). The water surface area of Bear Creek is 100 acres (2%). Table 1 shows the land use of the Bear Creek watershed.

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

| Region                           | Forest/Herbaceous | Mixed<br>Agriculture | Urban | Water |
|----------------------------------|-------------------|----------------------|-------|-------|
| Inner Harbor/Northwest<br>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 provinces of Central Maryland. The surficial geology of the Piedmont has been formed from the decomposition of various sedimentary, metamorphic, and igneous rocks. The underlying rock formations consist of schist, limestone, marble, and gneiss. The stream valleys along the fall line between the Piedmont and the Coastal Plain are typified by exposed igneous rocks such as gneiss and Baltimore gabro. 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 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 thick, 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 four general categories: urban; water; mixed agriculture; and forest/vegetation. Urban land-use categories represent 76% of the Inner Harbor/Northwest Branch and 91% of the Bear Creek watershed, respectively.

# 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 Cr III and Cr VI 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 water quality criterion, based on chronic toxicity, for Cr VI in saltwater is  $50\mu g/L$  and freshwater is  $11\mu g/L$  (COMAR 26.08.02.03-2G). The Inner Harbor/Northwest Branch segment is defined in COMAR 26.08.02.03-1B as freshwater. Of the two chromium species of concern, Cr III and Cr VI, Cr VI is highly toxic and therefore has a numeric criterion that is more stringent (i.e., at a lower concentration). Therefore, the Cr VI data will be evaluated against the Cr VI water quality standard to determine if there is a water quality impairment in either the Inner Harbor/Northwest Branch or Bear Creek.

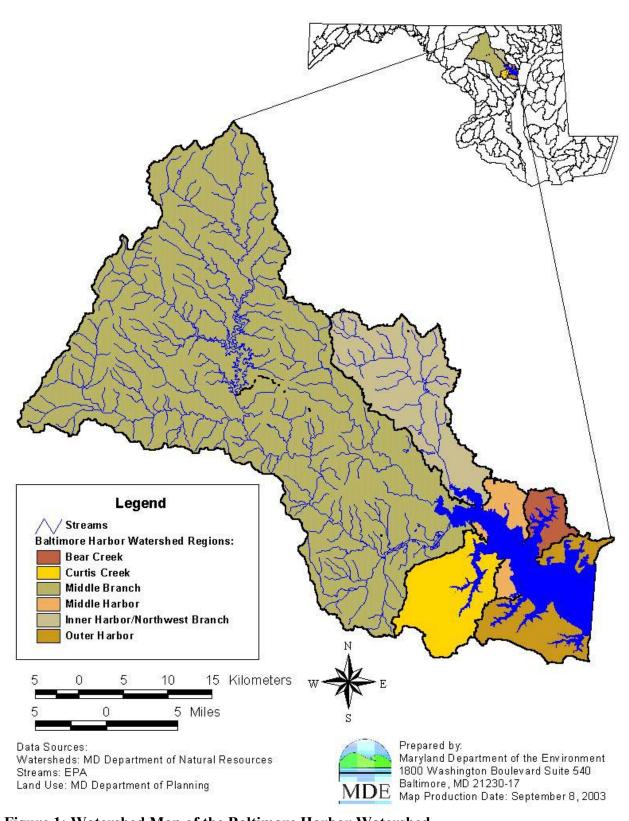


Figure 1: Watershed Map of the Baltimore Harbor Watershed

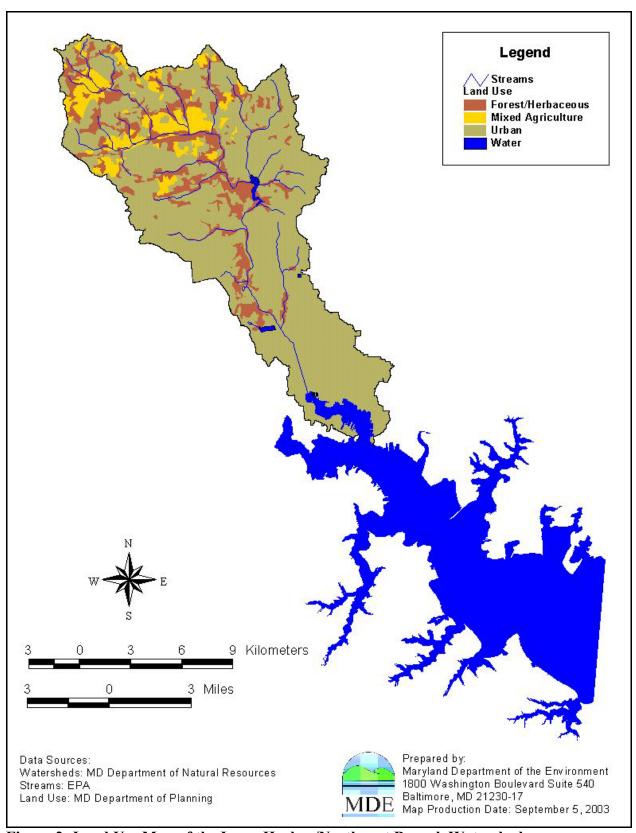


Figure 2: Land Use Map of the Inner Harbor/Northwest Branch Watershed

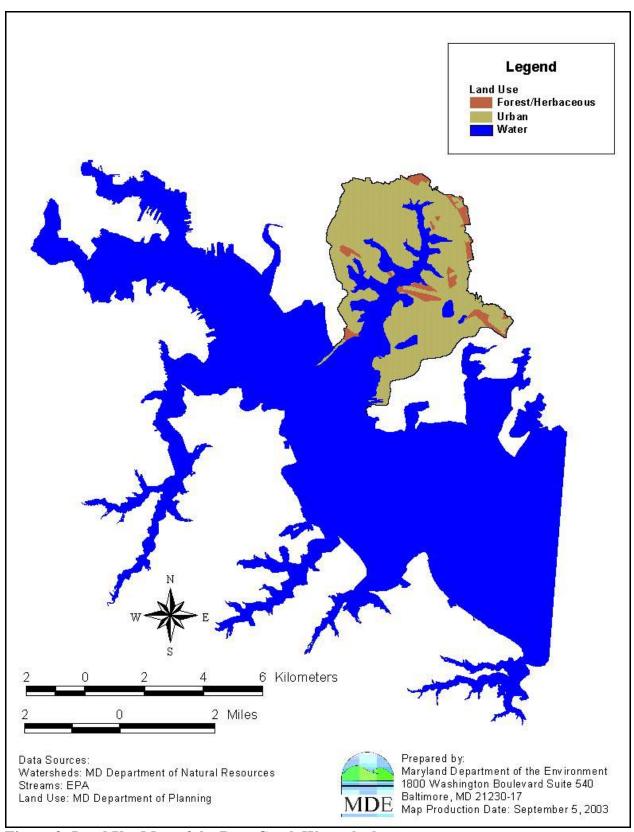


Figure 3: Land Use Map of the Bear Creek Watershed

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 during August 2003 (See Figure 4 and Tables 2 and 3). The data from this sampling effort is used to support this WQA. For each sample, concentrations were determined for: 1) dissolved Cr in the water column (1 meter from the bottom), and the surficial sediment pore water; 2) Cr III and Cr VI in the water column (1 meter from the bottom), and the surficial sediment pore water; 3) total Cr, 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 Cr VI do not exceed the water quality criteria for Cr VI in either the water column or the surficial sediment pore water.

The sediment data presented in Section 3.2, Table 7 and Table 8, indicates that high concentrations of total Cr remain present in the surficial sediments. However, using a molar-based analysis 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 the Cr present in the sediment from Cr VI to Cr III.

The ambient sediment bioassay data presented in Section 3.3, Tables 9 and 10 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 chemical contaminants at elevated levels in the sediment and pore water concentrations of Cr VI that indicate that this metal does not exceed the applicable water quality standard, MDE is unable to assign the cause of the toxicity to Cr VI.

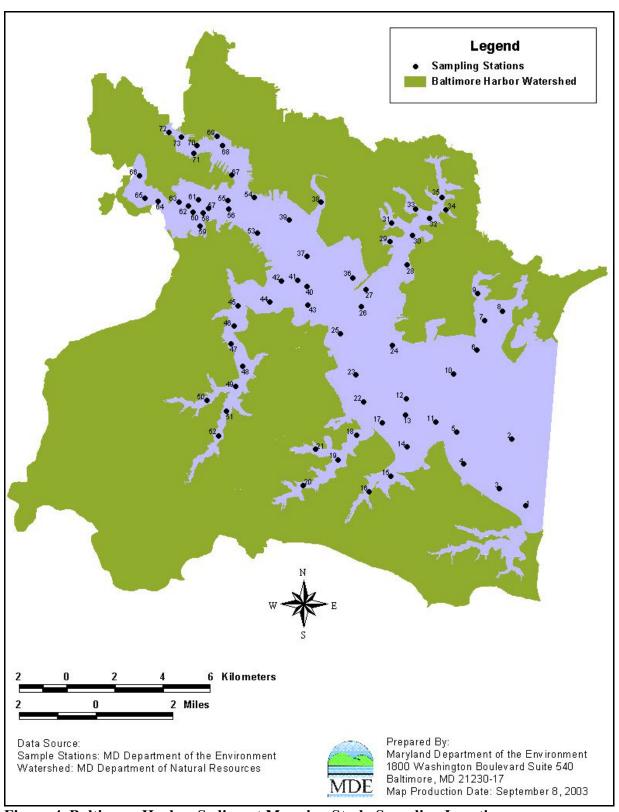


Figure 4. Baltimore Harbor Sediment Mapping Study Sampling Locations

# 3.1 WATER COLUMN EVALUATION

To evaluate the water quality of the Inner Harbor/Northwest Branch and Bear Creek, MDE evaluated the pore water concentrations of Cr VI against the freshwater and saltwater aquatic life chronic criteria for Cr VI 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 | <b>GPS Coordinates</b> | Station Description        |
|------------|------------------------|----------------------------|
| BSM 68     | 39.278                 | Southeast of Fells Pt.     |
|            | 76.583                 |                            |
| BSM 69     | 39.282                 | Southeast of Fells Pt.     |
|            | 76.586                 |                            |
| BSM 70     | 39.278                 | South of former chromium   |
|            | 76.596                 | refinery                   |
| BSM 71     | 39.275                 | Across channel from former |
|            | 76.598                 | chromium refinery          |
| BSM73      | 39.283                 | Head of Inner Harbor       |
|            | 76.609                 |                            |

**Table 3: Water Quality Analysis Stations for Bear Creek** 

| Station ID | <b>GPS Coordinates</b> | Station Description              |
|------------|------------------------|----------------------------------|
| BSM 28     | 39.233                 | Mouth of Bear Creek near         |
|            | 76.495                 | International Steel              |
| BSM 29     | 39.242                 | Cove Northwest of Route 695      |
|            | 76.503                 | bridge                           |
| BSM 30     | 39.244                 | Mid Creek adjacent to railroad   |
|            | 76.492                 | bridge                           |
| BSM 31     | 39.248                 | Head of small tributary entering |
|            | 76.502                 | Creek at railroad bridge         |
| BSM32      | 39.250                 | Head of Bear Creek/South of      |
|            | 76.484                 | 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 collection of porewater was conducted in an anoxic environment to maintain the appropriate sediment chemistry. The porewater was separated from the surficial sediments by centrifugation, filtered to remove particulate matter, and split for separate analysis. One half of the filtrate was analyzed for the free ionic species of Cr III and Cr VI using an ion chromatography method to separate Cr III and Cr VI ions from the remaining

matrix. Following the chromatographic separation step the sample was analyzed using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) to determine the concentrations of Cr III and Cr VI (Gurleyk).

The second half of the filtrate was analyzed for total Cr in the dissolved phase using a standard metals ICP-MS analysis. The values generated from both analyses were then assessed against the water quality criteria to determine if a violation of the water quality standard occurred. The Cr III, Cr VI, and Total Cr data from the water column and porewater are presented in Table 5 and Table 6. The detection limits for metals analysis are displayed in Table 4.

**Table 4: Chromium Analysis Detection Limits** 

| Analyte             | <b>Detection Limit</b> |
|---------------------|------------------------|
| Cr III Water Column | 0.017 μg/L             |
| Cr VI Water Column  | 0.022 μg/L             |
| Total Cr Sediment   | 0.50 mg/Kg DW          |

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

| Station | Water    | Column  | Pore Water |         |
|---------|----------|---------|------------|---------|
|         | Cr (III) | Cr (VI) | Cr (III)   | Cr (VI) |
|         | μg/L     |         | μg/L       |         |
| BSM68   | 0.222    | 0.279   | 0.07       | ND      |
| BSM69   | 0.129    | 0.163   | 0.31       | ND      |
| BSM70   | 0.125    | 0.262   | 0.50       | ND      |
| BSM71   | 0.109    | 0.131   | 0.50       | ND      |
| BSM73   | 0.070    | 0.178   | 0.36       | ND      |

Cr VI Chronic WQ Criteria for Freshwater =  $11 \mu g/L$ 

ND = Non Detect

Table 6: Bear Creek Water Column and Porewater Data

| Station | Water Column |         | Pore Water |         |
|---------|--------------|---------|------------|---------|
|         | Cr (III)     | Cr (VI) | Cr (III)   | Cr (VI) |
|         | μg/L         |         | μ          | g/L     |
| BSM28   | 0.263        | 0.176   | 0.05       | ND      |
| BSM29*  | 0.171        | 0.175   | 0.12       | ND      |
| BSM30   | 0.355        | 0.143   | 0.09       | ND      |
| BSM31   | 0.138        | 0.168   | 0.12       | ND      |
| BSM32*  | 0.132        | 0.148   | 0.17       | ND      |

\*Value is average of duplicate samples

Cr VI Chronic WQ Criteria for Saltwater = 50 µg/L

ND = Non Detect

# 3.2 SEDIMENT CHEMISTRY EVALUATION

To evaluate the sediment conditions, surficial (top 2 cm) sediment samples were collected by CBL in 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 total Cr, AVS-SEM, and sulfides. The results of the analysis are presented in Table 7 and Table 8.

Table 7: Inner Harbor/Northwest Branch Sediment Data\*

| Station | Total Cr   | AVS/SEM<br>Cr | AVS/SEM<br>Divalent Metals<br>Cu, Cd, Zn, Pb | AVS     | Excess<br>Sulfides |
|---------|------------|---------------|----------------------------------------------|---------|--------------------|
|         | mg/Kg DW** | μmole/g       | μmole/g                                      | μmole/g | μmole/g            |
| BSM68   | 443        | 1.60          | 7.46                                         | 78.75   | 69.69              |
| BSM69   | 480        | 2.11          | 7.91                                         | 369.38  | 359.36             |
| BSM70   | 1,068      | 4.66          | 7.59                                         | 173.44  | 161.19             |
| BSM71   | 1,286      | 6.60          | 10.78                                        | 196.88  | 179.50             |
| BSM73   | 500        | 2.01          | 7.13                                         | 236.25  | 227.11             |

<sup>\*</sup>The analysis is presented on a molar basis to account for the various molecular weights of the analytes.

**Table 8: Bear Creek Sediment Data\*** 

| Station  | Total Cr<br>mg/Kg DW** | AVS/SEM<br>Cr<br>µmole/g | AVS/SEM Divalent Metals Cu, Cd, Zn, Pb  µmole/g | AVS<br>µmole/g | Excess<br>Sulfides<br>µmole/g |
|----------|------------------------|--------------------------|-------------------------------------------------|----------------|-------------------------------|
| BSM28    | 705                    | 6.92                     | 19.42                                           | 144.06         | 117.72                        |
| BSM29*** | 724                    | 6.20                     | 21.29                                           | 304.06         | 276.58                        |
| BSM30    | 827                    | 10.80                    | 31.58                                           | 340.63         | 298.25                        |
| BSM31    | 847                    | 4.73                     | 19.14                                           | 500.00         | 476.13                        |
| BSM32    | 601                    | 6.00                     | 19.78                                           | 375.00         | 349.22                        |

<sup>\*</sup>The analysis is presented on a molar basis to account for the various molecular weights of the analytes.

<sup>\*\*</sup>DW = Dry Weight

<sup>\*\*</sup>DW = Dry Weight

<sup>\*\*\*</sup>Value is average of duplicate samples

Baltimore Harbor sediments are acted upon by chemical reactions that result in Cr being sequestered into non-reactive forms. The presence of a low dissolved oxygen environment with high levels of sulfides produces a reduction-based conversion of Cr VI to Cr III and the formation of Cr oxides and hydroxides. The sediment data presented above indicates that there are sulfides present in the sediment in concentrations well in excess of what would be required to reduce all chromium in the sediment from Cr VI to Cr III. As a result of the conversion to Cr III the porewater concentrations are below water quality criteria even though the bulk sediment concentrations are in excess of ERM levels (Boothman et al., 2000 and Berry et al., 2002).

#### 3.3 SEDIMENT TOXICITY EVALUATION

To complete the WQA, sediment toxicity 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 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 9 and Table 10.

Table 9: Inner Harbor/Northwest Branch Sediment Toxicity Data

| Station | Percent  | Growth                | Reproduction        |
|---------|----------|-----------------------|---------------------|
|         | Survival | mg/ind/d <sup>1</sup> | (Neonates/survivor) |
| 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      | 0.021                 | 0.30                |
| BSM73*  | 55       | 0.054                 | 0.94                |

<sup>&</sup>lt;sup>1</sup>Growth rate equals milligram dry weight/individual/day

<sup>\*</sup>Significant observed toxicity

| Station | Percent  | Growth                | Reproduction        |
|---------|----------|-----------------------|---------------------|
|         | Survival | mg/ind/d <sup>1</sup> | (Neonates/survivor) |
| 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                |

**Table 10: Bear Creek Sediment Toxicity Data** 

The endpoints for the 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 sites showed a significant reduction in survival except for BSM 31 (Table 10). 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 rate at this site, there was a reduction in reproduction (Table 10).

All of the sediments from the tested sites showed significant reductions in test endpoints. BSM sites 28, 29, 30, 32, 68, 69, 70, 71, and 73 showed reduced survival of *L. plumulosus*. 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). The only station not having significant survival effects on the amphipod was BSM 31. 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 indicates that the pore water and water column data collected for Cr VI does not exceed the water quality standard in the water column. The toxicity data indicates mortality in 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) has produced sulfide concentrations within the sediments that are at levels well in excess of what would be needed to convert the Cr present in the Northwest Branch/Inner Harbor and Bear Creek sediments from Cr VI to Cr III and render

<sup>&</sup>lt;sup>1</sup>Growth rate equals milligram dry weight/individual/day

<sup>\*</sup>Significant observed toxicity

it unavailable to partition into the pore water in quantities that would exceed water quality standards. As a result, the sediment chemistry present in the Northwest Branch/Inner Harbor and Bear Creek creates an environment where Cr cannot be determined as the specific cause of the observed toxicity.

Therefore, barring any contradictory data, this information provides sufficient justification to remove Cr from Maryland's 303(d) list as an impairing substance in the Inner Harbor/Northwest Branch and Bear Creek. The segments will continue to be listed for biological impacts due to sediment toxicity based on the data collected in the WQA effort. To address the toxicity impairment, MDE will begin the process of developing a field study 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.

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