Water Quality Analysis of Cadmium, Chromium, Copper, and Lead in the Potomac River Middle Tidal, Charles County, Maryland

FINAL

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CBL	Chesapeake Biological Laboratory
Cd	Cadmium
COMAR	Code of Maryland Regulations
Cr	Chromium
Cu	Copper
CWA	Clean Water Act
DNR	Department of Natural Resources
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency
HAC	Hardness Adjusted Criteria
HACC	Hardness Adjusted Chronic Criteria
LSD	Least Significant Difference
MDE	Maryland Department of the Environment
MDL	Method Detection Limit
MDP	Maryland Department of Planning
MRLC	Multi Resolution Land Cover
mg/l	Milligrams per Liter
μg/l	Micrograms per Liter
NPDES	National Pollution Discharge Elimination System
NWS	National Weather Service
Pb	Lead
PCBs	Polychlorinated Biphenyls
ppt	Parts per Thousand
SCS	Soil Conservation Service
SHA	State Highway Administration
SSURGO	Soil Survey Geographic
TMDL	Total Maximum Daily Load
ug/l	Micrograms per Liter
UMCES	University of Maryland Center for Environmental Science
USGS	United States Geological Survey
WQA	Water Quality Analysis
WQLS	Water Quality Limited Segment
WWTP	Wastewater Treatment Plant

EXECUTIVE SUMMARY

Section 303(d) of the federal Clean Water Act (CWA) and the 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) for the specified substance that the waterbody can receive without violating water quality standards, or demonstrate that water quality standards are being met.

Potomac River Middle Tidal (basin code 02-14-01-02), located in Charles County, MD, was identified on the State's list of WQLSs as impaired by nutrients (1996 listing), suspended sediments (1996 listing), cadmium (Cd), (1996 listing), chromium (Cr), (1996 listing), copper (Cu), (1996 listing), lead (Pb) (1996 listing), polychlorinated biphenyls (PCBs), (2002 listing), and impacts to biological communities (2004 listing). All impairments were listed for the tidal waters except for impacts to biological communities, which are listed for the tidal and non-tidal region. Code of Maryland Regulations (COMAR) 26.08.02.03-1-B(3)(m)(i) defines the tidal Potomac River upstream of Upper Cedar Point, MD which includes the Potomac River Middle Tidal, as a fresh waterbody. This report provides an analysis of recent monitoring data, including hardness data, which shows that the aquatic life criteria for Cd, Cr, Cu, and Pb are being met in the Potomac River Middle Tidal.

The analyses support the conclusion that TMDLs for Cd, Cr, Cu, and Pb are not necessary to achieve water quality standards. Barring the receipt of any contradictory data, this report will be used to support the Cd, Cr, Cu, and Pb listing change for the Potomac River Middle Tidal from Category 5 ("waterbodies impaired by one or more pollutants and requiring a TMDL") to Category 2 ("surface waters that are meeting some standards and have insufficient information to determine attainment of other standards") when MDE proposes the revision of Maryland's 303(d) list for public review in the future. The listings for nutrients, suspended sediments, PCBs, and impacts to biological communities will be addressed separately at a future date. Although the waters of the Potomac River Middle Tidal watershed do not display signs of toxic impairments due to Cd, Cr, Cu, or Pb, the State reserves the right to require additional pollution controls in the Potomac River Middle Tidal watershed if evidence suggests that metals from the basin are contributing to downstream water quality problems.

FINAL

1.0 INTRODUCTION

Section 303(d) of the federal Clean Water Act (CWA) and 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. 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) for 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 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 criteria; 3) refinements to water quality criteria, or the interpretation of those standards, which result in standards being met; or 4) correction to errors made in the initial listing.

Potomac River Middle Tidal (basin code 02-14-01-02) was identified on the State's 1996 303(d) list as impaired by nutrients, suspended sediments, cadmium (Cd), chromium (Cr), copper (Cu), and lead (Pb), with additional listings of polychlorinated biphenyls (PCBs) in fish tissue in 2002, and impacts to biological communities in 2004. All impairments were listed for the tidal waters except for the impacts to biological communities, which are listed for the tidal and non-tidal segments. The Code of Maryland Regulations (COMAR, 26.08.02.03-1B(3)(m)(i)) defines the Potomac River upstream of the line connecting Upper Cedar Point, MD and Chotank Creek, VA as freshwater. The waterbody is below the head of tide, so there is tidal influence, but because the watershed area flowing to the Potomac River is so large, the freshwater influence is dominant. The Maryland Surface Water Use Designation (COMAR 26.08.02.08N) for the Potomac River Middle Tidal is Use II - migratory spawning and nursery use (February 1 to May 31), shallow water submerged aquatic vegetation use (April 1 to October 30) and shellfish harvesting use (January 1 to December 31).

The metals listings in Maryland's 2004 303(d) list of impaired waterbodies are based on the 1996 305(b) report by Maryland Department of Natural Resources (DNR). The informational basis for this listing is the Maryland Department of the Environment (MDE) 1988 304(l) list, which states that the tidal Potomac River segment in this watershed exceeds the EPA chronic aquatic life criteria for Cd, Cr, Cu, and Pb. This report considers recent data to establish whether an impairment currently exists.

A Water Quality Analysis (WQA) of Cd, Cr, Cu, and Pb for the Potomac River Middle Tidal was conducted by MDE using recent water column chemistry data and sediment toxicity data. A data solicitation for these metals was conducted by MDE and all readily available data from the past five years was considered. A water quality survey was conducted in the spring of 2005 by MDE with the assistance of the University of Maryland Center for Environmental Studies (UMCES) to assess the level of metals and toxics contamination in the tidal Potomac River.

The remainder of this report lays out the general setting of the waterbody within the Potomac River Middle Tidal watershed, presents a discussion of the water quality characterization process, and provides conclusions with regard to the characterization. The listings for suspended sediments, nutrients, PCBs, and impacts to biological communities will be addressed separately at a future date.

2.0 GENERAL SETTING

The Potomac River Middle Tidal watershed is located in the central Maryland tidal region of the Potomac River (Figure 1). It is located in Charles County and the river segment extends from Marshall Hall, MD downstream to Smith Point, MD. The tidal segment of the Potomac River Middle Tidal differs from a true estuary in that there is little intrusion of salt from the lower Chesapeake Bay for the majority of the year; thus, there is neither longitudinal nor lateral distribution of salinity. This atypical tidal exchange produces unusual salinity distributions within the Potomac River Middle Tidal basin. Low salinity is primarily attributable to the heavy freshwater input from the upstream Potomac River and other tributaries which discharge directly to the Potomac River Middle Tidal basin. The watershed area of the upstream Potomac River that drains to this watershed is approximately 12,540 square miles.

The watershed is mostly undeveloped forestland (Figure 2). Agricultural operations are minimal and localized. Limited rural residential uses are present, and the only urban center is the town of Indian Head, where industrial and commercial development and the Indian Head Wastewater Treatment Plant (WWTP) are located. Naval District Wasington-Indian Head has several facilities located in the Middle Potomac River Tidal watershed area, and several facilities have permitted discharges to the Potomac River Middle Tidal waters.

The Potomac River Middle Tidal watershed is located entirely in the Coastal Plains province. The topography is characterized as nearly level to moderately sloped. The soils are generally characterized as moderately drained, loamy soils, with a clayey sub-soil (Natural Resources Conservation Service, 1974).

The Potomac River mainstem within the watershed is approximately 21 miles (33.8 km) in length, extending from Marshall Hall, MD to Smith Point, MD. The Potomac River Middle Tidal watershed has an area of approximately 20,878 acres (non-water) or 32.6 square miles. The land uses in the watershed consist of forest and other herbaceous (16,642 acres or 77.6%), urban (1,920 acres or 12.3%), mixed agriculture (1,778 acres or 7.0%), and wetlands (638 acres or 3.0%). These land uses are based on 2000 Maryland Department of Planning (MDP) land use/land cover data.

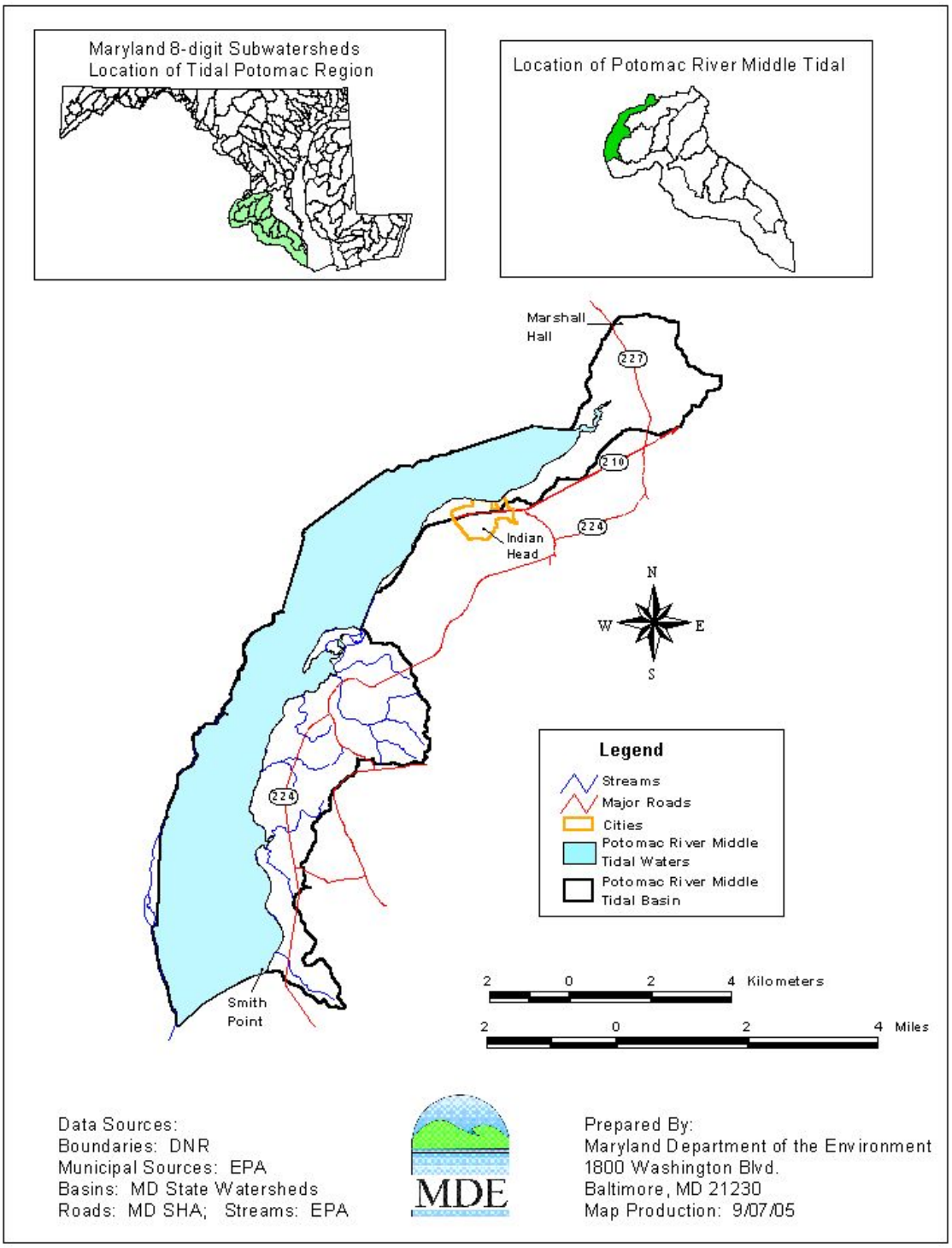

Figure 1: Location Map of the Potomac River Middle Tidal Drainage Basin

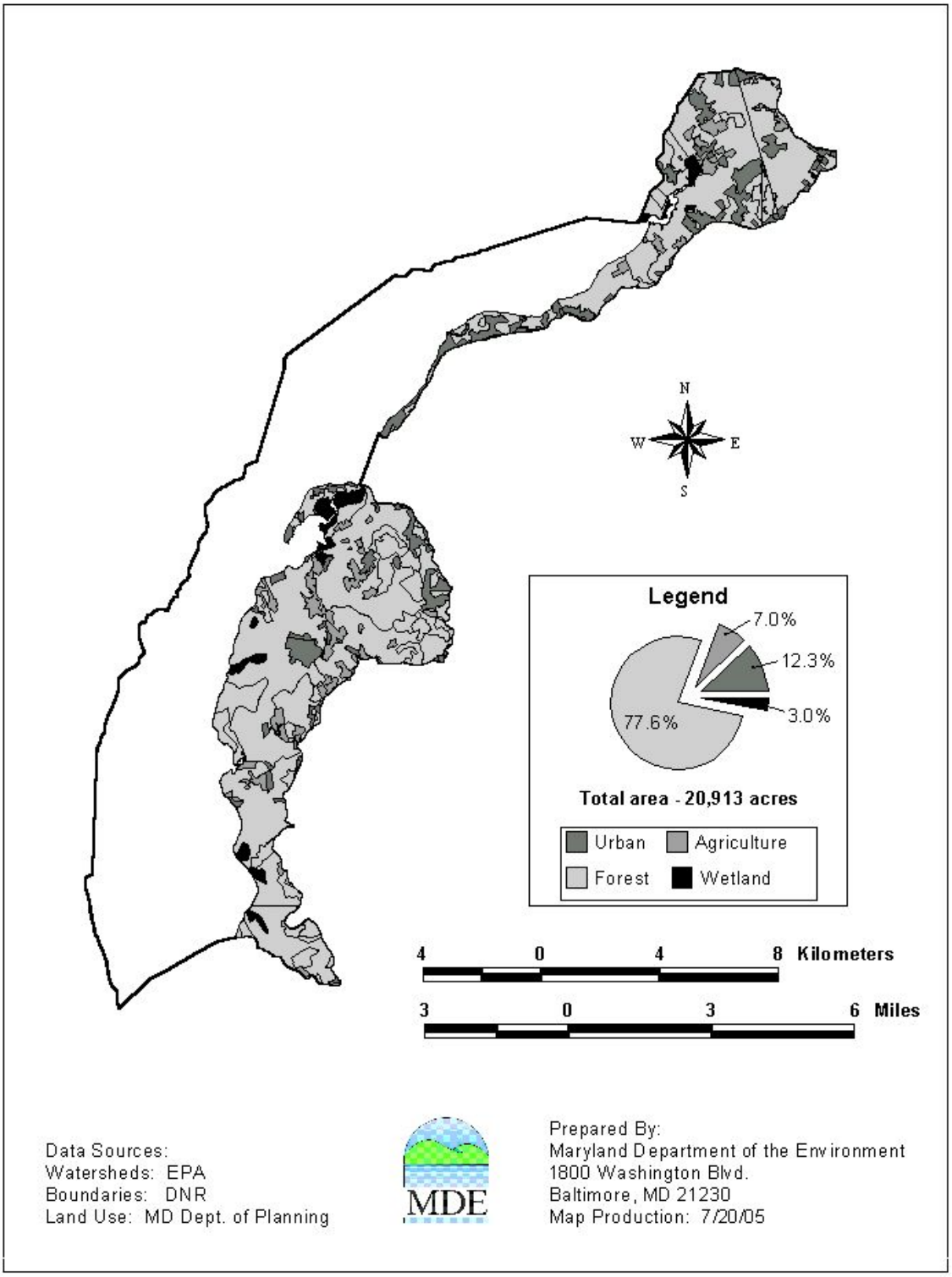

Figure 2: Land Use Map of the Potomac River Middle Tidal Drainage Basin

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 different designated uses may differ and are dependent on the specific designated use(s) of a waterbody. Maryland's water quality standards presently include numeric criteria for metals and other toxic substances based on the need to protect aquatic life, wildlife and human health. Water quality standards for toxic substances also address sediment quality to ensure the bottom sediment of a waterbody is capable of supporting aquatic life, thus protecting the designated uses.

The Maryland Surface Water Use Designation (COMAR 26.08.02.08N) for the Potomac River Middle Tidal is Use II - migratory spawning and nursery use (February 1 to May 31), shallow water submerged aquatic vegetation use (April 1 to October 30) and shellfish harvesting use (January 1 to December 31). In addition, COMAR requires that all waterbodies in the state of Maryland support a Use I designation (water contact recreation, fishing, and protection of aquatic life and wildlife). Code of Maryland Regulations 26.08.02.03-1(B)(3)(m)(i) defines the tidal region of the Potomac River basin considered in this WQA as being freshwater. Salinity concentrations for the Potomac River Middle Tidal are below 1ppt, thus it is a freshwater body and freshwater criteria are applied. The freshwater aquatic life criteria (based on a default hardness value of 100 mg/L) for Cd, Cr, Cu, and Pb are displayed in Table 1 (COMAR 26.08.02.03-2G(1)). The water column data presented in Section 3.1, Table 4, shows that concentrations of Cd, Cr, Cu, and Pb in the water column do not exceed non-hardness adjusted water quality criteria.

Table 1: Water Quality Criteria for Metals

Metal	Fresh Water Aquatic Life Acute Criteria (µg/L)*	Fresh Water Aquatic Life Chronic Criteria (µg/L)*	Human Health Criteria Fish Consumption (µg/L)
Cd	2	0.25	
Cr (III)	570	74	
Cu	13	9	1300
Pb	65	2.5	

*Criteria based on default hardness of 100 mg/L

A water column survey used to support this WQA was conducted by the University of Maryland Center for Environmental Science (UMCES) at seven stations throughout the Potomac River Middle Tidal estuary on April 13, 2004. Table 2 shows the list of stations with their geographical coordinates. The station locations are presented in Figure 3.

Table 2: Sample Stations for Potomac River Middle Tidal

Station ID	GPS coordinates	Station Description
MDE1	38.41 -77.29	Potomac River Mainstem
MDE2	38.49 -77.31	Potomac River Mainstem off Quanitco Creek
MDE3	38.50 -77.30	Potomac River Mainstem off Quanitco Creek, near Chopawamsic Island
MDE4	38.56 -77.20	Mouth of Mattawoman Creek
MDE5	38.62 -77.21	Occoquan Bay
SanPR07	38.53 -77.27	Potomac River Mainstem at Moss Point
SanPR08	38.60 -77.17	Potomac River Mainstem near Indian Head

An ambient sediment bioassay was conducted by the University of Maryland Wye Research and Education Center in the Potomac River Middle Tidal basin. Sediment bulk samples were collected at each of the seven stations shown in Table 2 and Figure 3. The sediment bioassay was conducted using a standard EPA 10 day amphipod test. Results of the toxicity test in the watershed exhibit normal survival and growth rate with respect to the control. Sediment samples would have been analyzed for metals chemistry if the sediments were found to be toxic. Table 6 in Section 3.2 shows the results of the sediment toxicity test.

For the water quality evaluation, a comparison is made between dissolved metals water column concentrations and the fresh water aquatic life chronic criteria, the most stringent of the numeric water quality criteria for each of the metals. Water hardness concentrations were obtained for each station to adjust the fresh water aquatic life criteria that were listed based on a default hardness of 100 mg/l.

MDE calculates fresh water aquatic life criteria as a function of a hardness adjustment formula for metals where toxicity is a function of total hardness. According to EPA's National Recommended Water Quality Criteria (EPA, November 2002), allowable hardness values must fall within the range of 25 - 400 mg/L. When the measured hardness exceeds 400 mg/l, MDE will use this value as an upper limit when calculating the hardness adjusted criteria (HAC). Based on technical information, EPA's Office of Research and Development does not recommend a lower limit on hardness for adjusting criterion (EPA, July 2002). A lower limit may result in criteria that is less protective of the water quality standard. In analyses where available hardness data indicates a value below 25 mg/L, MDE may perform additional analyses to insure data quality objectives for the assessments were met. When data is of questionable quality, MDE will take additional samples to establish the validity of the initial assessment.

The HAC equation for metals is as follows (EPA, 2002):

$HAC = e^{(m[\ln (Hardness(mg/l))]+b)} * CF$

Where,
HAC = Hardness Adjusted Criteria (µg/l)
m = slope
b = y intercept
CF = Conversion Factor (conversion from totals to dissolved numeric criteria)

The chronic and acute HAC parameters for Cd, Cr, Cu, and Pb are presented in Table 3 (EPA, 2002).

Table 3: HAC Parameters (Fresh Water Aquatic Life Criteria)

	Chronic Parameters			Acute Parameters		
Metal	**Slope (m)**	**y Intercept (b)**	**Conversion Factor (CF)**	**Slope (m)**	**y Intercept (b)**	**Conversion Factor (CF)**
Cd	0.741	-4.719	1.102-ln(hardness)*0.041838	1.017	-3.924	1.136672-ln(hardness)*0.041838
Cr	0.819	0.685	0.86	0.819	3.726	0.316
Cu	0.855	-1.702	0.96	0.942	-1.700	0.960
Pb	1.273	-4.705	1.46203-ln(hardness)*0.145712	1.273	-1.460	1.46203-ln(hardness)*0.145712

3.1 WATER COLUMN EVALUATION

A data solicitation for metals was conducted by MDE, and all readily available data from the past five years was considered in the WQA. The water column data is presented in Table 4 for each station and is evaluated using the fresh water hardness adjusted chronic criteria (Baker, 2004). Table 4 displays hardness (mg/L), hardness adjusted chronic criteria (HACC, µg/L), and sample concentration (µg/L). The metals water column data is also presented in Figures 4-7. Table 5 shows the method detection limits for each metal.

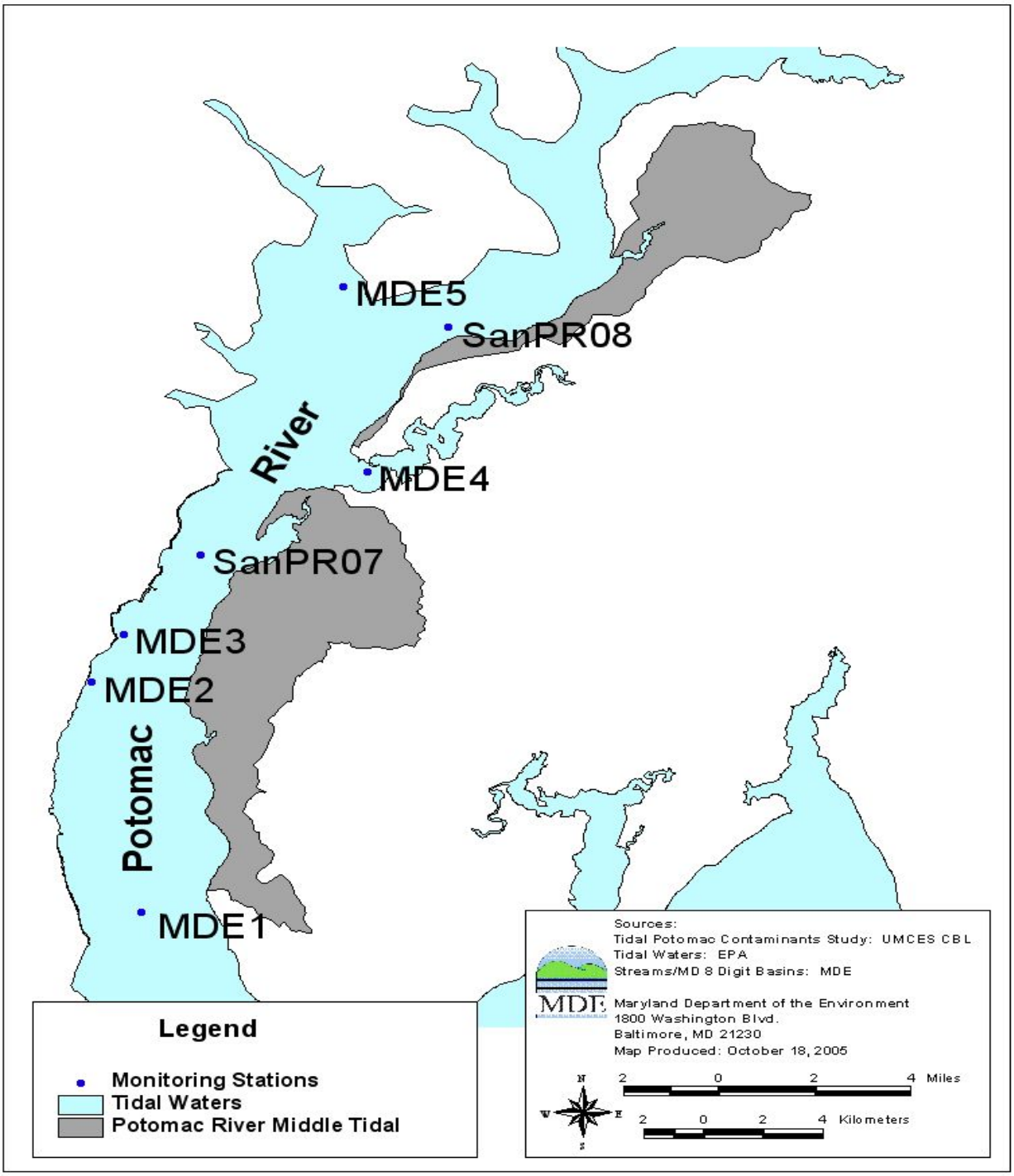

Figure 3: Potomac River Middle Tidal Sample Station Location Map

Table 4: Potomac River Middle Tidal Water Column Data

		Cd		Cr		Cu		Pb	
Station	**Hardness**	**Criteria (µg/L)**	**Sample (µg/L)**	**Criteria (µg/L)**	**Sample (µg/L)**	**Criteria (µg/L)**	**Sample (µg/L)**	**Criteria (µg/L)**	**Sample (µg/L)**
MDE1	37.36	0.12	0.011	33.09	0.1	3.86	1.75	0.85	0.137
MDE2	36.74	0.12	0.007	32.64	0.2	3.81	2.17	0.83	0.135
MDE3	36.74	0.12	0.006	32.64	0.2	3.81	1.91	0.83	0.154
MDE4	36.74	0.12	0.006	32.64	0.1	3.81	1.29	0.83	0.07
MDE5	36.68	0.12	0	32.60	0.2	3.80	2.02	0.83	0.253
SanPR07	39.76	0.13	0	34.82	0.2	4.07	1.63	0.91	0.107
SanPR08	42.41	0.14	0	36.71	0.1	4.30	1.27	0.98	0.071

* Fresh Water Aquatic Life Chronic Criterion (hardness adjusted)
ND - Not detected

Hardness ranged from 36.68 mg/l to 42.41 mg/l. The observed concentrations for Cd in the water column were generally an order of magnitude lower than their respective hardness-adjusted freshwater chronic criteria. The observed concentrations for Cr in the water column were two orders of magnitude lower than their respective freshwater hardness-adjusted chronic criteria (HACC). The observed concentrations for Cu and Pb in the water column were generally less than half of their respective hardness-adjusted freshwater chronic criteria.

Table 5: Metals Method Detection Limits

Metal	Detection Limit (mg/L)
Cd	0.005
Cr	0.1
Cu	0.05
Pb	0.05

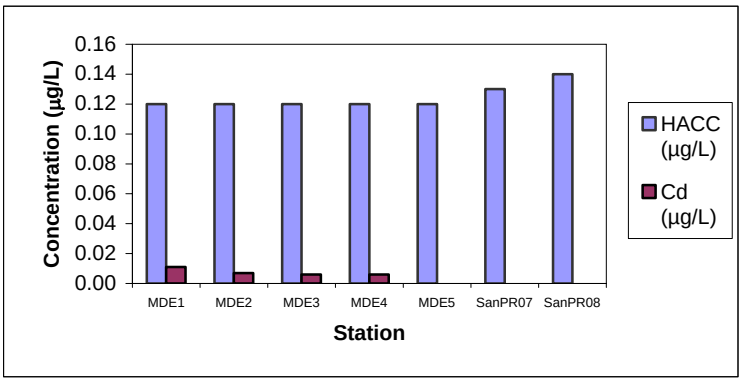

Figure 4: Potomac River Middle Tidal Water Column Data (Cd)

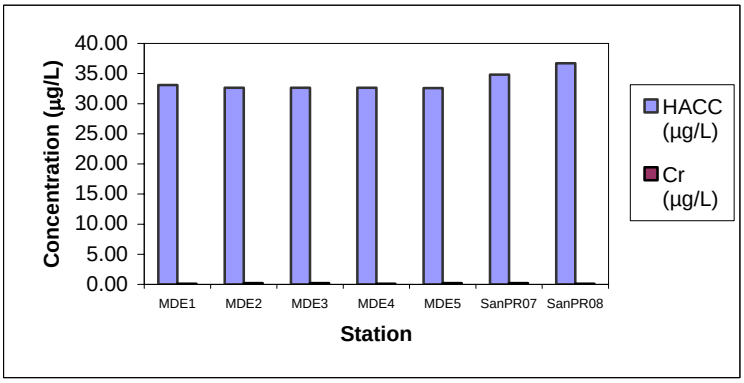

Figure 5: Potomac River Middle Tidal Water Column Data (Cr)

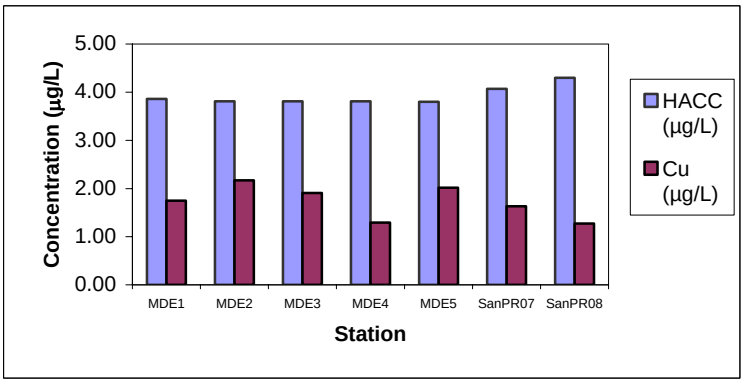

Figure 6: Potomac River Middle Tidal Water Column Data (Cu)

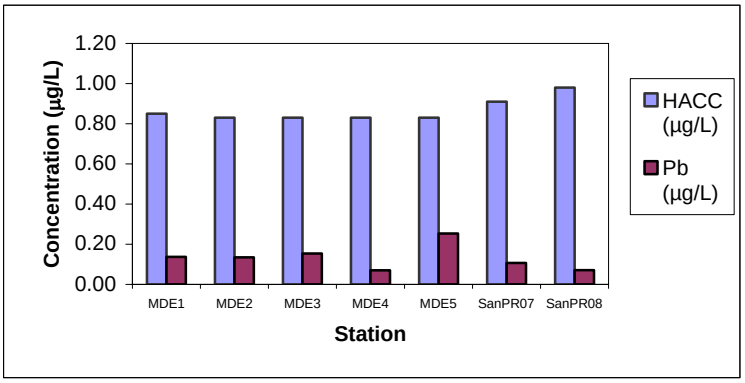

Figure 7: Potomac River Middle Tidal Water Column Data (Pb)

3.2 SEDIMENT QUALITY EVALUATION

Sediment quality in the Potomac River Middle Tidal basin was evaluated using a 10-day whole sediment test with the representative freshwater amphipod *Hyalella azteca* (Fisher, 2005*).* This species was chosen because of its ecological relevance to the waterbody of concern. *Hyalella azteca* is an EPA-recommended test species for assessing the toxicity of freshwater (EPA, 2001). Seven surficial sediment samples were collected April 13, 2005 using a petite ponar dredge (top 2 cm) in the Potomac River Middle Tidal basin. Control sediments were collected from the Wye River, from a depositional area previously characterized as low in contaminants (Fisher, personal communication, 2005). Refer back to Figure 3 for the station locations. The results are presented in Table 6. Five replicates containing twenty amphipods each were exposed to the sediment sample, as well as a control sediment, for testing. The table displays amphipod survival (%), and amphipod growth (mg dry weight).

Table 6: Results of Sediment Toxicity Test in the Potomac River Middle Tidal

Station	Average Amphipod Survival,%	Average Growth, final amphipod weight, mg
Control – Group 1	95.0	0.18
MDE 01	91.3	0.23
MDE 02	96.3	0.21
MDE 04	97.5	0.21
MDE 05	100.0	0.24
Control – Group 2	92.5	0.19
SanPR 07	98.8	0.25
SanPR 08	95.0	0.23

The test considers two performance criteria: survival and growth. For the test to be valid the average survival of control sample must be greater than 80%, and there must be measurable growth in the control samples.

Survival of amphipods in the field sediment samples was not significantly less than the average survival demonstrated in the control samples. The average survival for control samples in the test was 93.75%. The field sediment sample average survival results were no lower than 91.3%. No sediment samples in the Potomac River Middle Tidal exhibited toxicity contributing to mortality.

Average amphipod growth was similar to the control samples at all stations. The control samples exhibited an average final dry weight of 0.185 mg, in contrast to a minimum final weight among the field sediment samples of 0.21 mg. Given that the field sediment samples exhibited equal or more growth than the control sample, no samples exhibit toxicity contributing to growth inhibition.

Statistical analyses were performed on the toxicity test data to determine significant difference between the control and field samples. All survival proportion data were Arc Sine Square Root transformed prior to analyses. Alpha was 0.05 for all tests. All datasets were analyzed for normality (Chi-Square Test) and homogeneity of variance (Hartley's Test) prior to analyses. If the datasets were normal and homogeneous then they were analyzed by Analysis of Variance (ANOVA) followed by a Dunnett's Test to determine if there were significant reductions from the control endpoints. If the datasets were not normal or had heterogeneous variability then they were analyzed by the non-parametric Kruskal-Wallis' ANOVA by Ranks followed by a Dunn's Multiple Comparison Test to determine possible reductions in survival and growth from control survival and growth (Fisher, 2005).

4.0 CONCLUSION

The WQA establishes that the water quality criteria for Cd, Cr, Cu, and Pb are being achieved in the waterbody. Water column samples collected April 13, 2004 at seven monitoring stations in the Potomac River Middle Tidal basin demonstrate that numeric water quality criteria pertaining to the designated use are being met. Surficial sediment samples collected and used for bioassay toxicity tests demonstrate no impacts on amphipod survival or growth, therefore no sediment toxicity exists. Barring the receipt of any contradictory data, this report will be used to support the Cd, Cr, Cu, and Pb listing changes for the Potomac River Middle Tidal from Category 5 ('waterbodies impaired by one or more pollutants and requiring a TMDL") to Category 2 ("surface waters that are meeting some standards and have insufficient information to determine attainment of other standards") when MDE proposes the revision of Maryland's 303(d) list for public review in the future. The listings for nutrients, suspended sediments, PCBs, and impacts to biological communities will be addressed separately at a future date. Although the waters of the Potomac River Middle Tidal watershed do not display signs of toxic impairments due to Cd, Cr, Cu, or Pb, the State reserves the right to require additional pollution controls in the Potomac River Middle Tidal watershed if evidence suggests that metals from the basin are contributing to downstream water quality problems.

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