Water Quality Analysis of Cadmium in Lower Susquehanna River, Cecil and Harford County, Maryland

FINAL

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List of Abbreviations

AVS	Acid Volatile Sulfide
BDL	Below Detection Limit
CBL	Chesapeake Biological Laboratory
Cd	Cadmium
cm	Centimeter
COMAR	Code of Maryland Regulations
CWA	Clean Water Act
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency
ERL	Effects Range Low
ERM	Effects Range Median
HAC	Hardness Adjusted Criteria
LEL	Lowest-observed Effects Limit
LSD	Least Significant Difference
MDE	Maryland Department of the Environment
MDP	Maryland Department of Planning
MET	Minimum Effects Threshold
MRLC	Multi Resolution Land Cover
mg/l	Milligrams per Liter
NPDES	National Pollution Discharge Elimination System
NWS	National Weather Service
PCBs	Polychlorinated Biphenyls
PEC	Probable Effects Concentration
PEL	Probable Effects Limit
ppt	Parts per Thousand
SCS	Soil Conservation Service
SEL	Severe Effects Limit
SEM	Simultaneously Extracted Metals
SHA	State Highway Administration
SQG	Sediment Quality Guideline
SSURGO	Soil Survey Geographic
TEC	Threshold Effects Concentration
TEL	Threshold Effects Limit
TET	Toxic Effects Threshold
TMDL	Total Maximum Daily Load
UMCES	University of Maryland Center for Environmental Sciences
USGS	United States Geological Survey
WER	Water Effects Ratio
WQA	Water Quality Analysis
WQLS	Water Quality Limited Segment
µg/l	Micrograms per Liter

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.

Lower Susquehanna River (basin code 02120201), located in Cecil and Harford County, was identified on the State's list of WQLSs as impaired by nutrients (1996 listing), suspended sediments (1996 listing), cadmium (Cd) (1996 listing), polychlorinated biphenyls (PCBs) in fish tissue (2002 listing), and evidence of impacts to biological communities (2002 listing). The biological impairments listing is designated for two non-tidal streams, Herring Run and an unnamed tributary of the Lower Susquehanna River, while the remaining listings apply to the tidal portion. Code of Maryland Regulations (COMAR) 26.08.02.03-1-B(3)(a) defines the Lower Susquehanna River, as a fresh waterbody. This report provides an analysis of recent monitoring data, including hardness data, which shows that the aquatic life criteria and designated uses associated with Cd are being met in the Lower Susquehanna River. In addition, the results of an ambient sediment bioassay conducted in Lower Susquehanna River, by the University of Maryland Wye Research Center, established that there is no toxicity in the sediment as a result of Cd or other toxics contamination. The information (P. Jiapizian, personal communication 2001) used for listing Cd is suspect due in part to sampling and analysis methods available at the time, and assessment inconsistencies that led to the listing in 1996.

This report provides an analysis of recent monitoring data, including hardness data, which shows that the aquatic life uses and criteria are being met in the Lower Susquehanna River watershed, and 303(d) impairment listings associated with Cd are not supported by the analyses contained herein. The analyses support the conclusion that a TMDL for Cd is not necessary to achieve water quality standards. Barring the receipt of contradictory data, this report will be used to support a Cd listing change for the Lower Susquehanna River from Category 5 ("waterbodies impaired by one or more pollutants requiring a TMDL") to Category 2 ("Surface waters that are meeting some standards and have insufficient information to determine attainment of other standards"), when the Maryland Department of the Environment (MDE) proposes the revision of Maryland's 303(d) list for public review in the future. The listings for suspended sediments, PCBs, and impacts to biological communities will be addressed separately at a future date. A WQA for nutrients was completed in 2005.

Although the waters of Lower Susquehanna River watershed do not display signs of toxic impairments due to Cd, the State reserves the right to require additional pollution controls in Lower Susquehanna watershed if evidence suggests that Cd from the basin is contributing to downstream water quality problems.

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.

Lower Susquehanna River (basin code 02120201) was identified on the State's 303(d) list as impaired by nutrients (1996), suspended sediments (1996), cadmium (Cd) (1996), polychlorinated biphenyls (PCBs) (2002) and for impacts to biological communities (2002). All impairments were listed for the tidal waters except for the impacts to biological communities, which are listed for the non-tidal region. Code of Maryland Regulations (COMAR) defines the Lower Susquehanna River, as a fresh water body.

The informational basis (P. Jiapizian, personal communication, 2001) for this listing contended that mean levels of Cd exceeded the EPA chronic aquatic life criteria at the time of listing (1996). Although criteria were "exceeded", several methodological flaws in the monitoring and listing assessment used in 1996 exist. First, unfiltered (total metals) samples were compared to dissolved criteria. Second, current criteria for Cd rely on a hardness correction – since no hardness data existed, criteria thresholds using a 100 mg/L "default" hardness value were used for the assessment. Finally, station means for each analyte were calculated setting non-detects at ½ the detection limit. While this procedure may have been appropriately conservative at the time, the sensitivity of analytical instrumentation has improved dramatically, and samples taken currently for Cd have appropriate detection limits that are well below their respective criteria values.

A Water Quality Analysis (WQA) of Cd for the tidal waters of Lower Susquehanna River was conducted by the Maryland Department of the Environment (MDE) using recent water column chemistry data, sediment 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. The listings for suspended sediments, PCBs, and impacts to biological communities will be addressed separately at a future date. A WQA for nutrients was completed in 2005.

The remainder of this report lays out the general setting of the waterbody within the Lower Susquehanna River watershed, presents a discussion of the water quality characterization process, and provides conclusions with regard to the characterization.

2.0 GENERAL SETTING

Lower Susquehanna River is located in Cecil and Harford County, Maryland and flows from the outlet of the Conowingo Dam south into the headwaters of the Chesapeake Bay. The Lower Susquehanna River, Deer Creek, Octoraro Creek, and Broad Creek are all part of the network of streams that make up the basin. Lower Susquehanna River is approximately 10 miles in length, with a watershed area of approximately 19,885 acres (Figure 1). The land uses in the watershed are mixed agricultural (5,719 mi or 28.8% of the area), forest (8,589 mi or 43.2 % of the area) and urban (5,577 mi or 28% of the area). Please refer to Figure 2 for a map of these land uses (MDP 2000).

The Lower Susquehanna River watershed is located in the extreme reaches of the Maryland Portion of the headwaters of the Chesapeake Bay watershed (Figure 1). It is located in Cecil and Harford County and is bounded by the Swan Creek watershed to the west and by the Northeast River to the east. Lower Susquehanna River is tidal (fresh) as far north as the Conowingo Dam. The tidal segment of the Lower Susquehanna River differs from a true estuary in that there is little intrusion of salt from the lower Chesapeake 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 Lower Susquehanna River.

The Lower Susquehanna River watershed lies within the Piedmont province in Central Maryland. The Piedmont province is characterized by gentle to steep rolling topography, low hills and ridges. The surficial geology is characterized by crystalline rocks of volcanic origin consisting primarily of schist and gneiss. These formations are resistant to short-term erosion and often determine the limits of stream bank and bed. (Coastal Environmental Services, 1995)

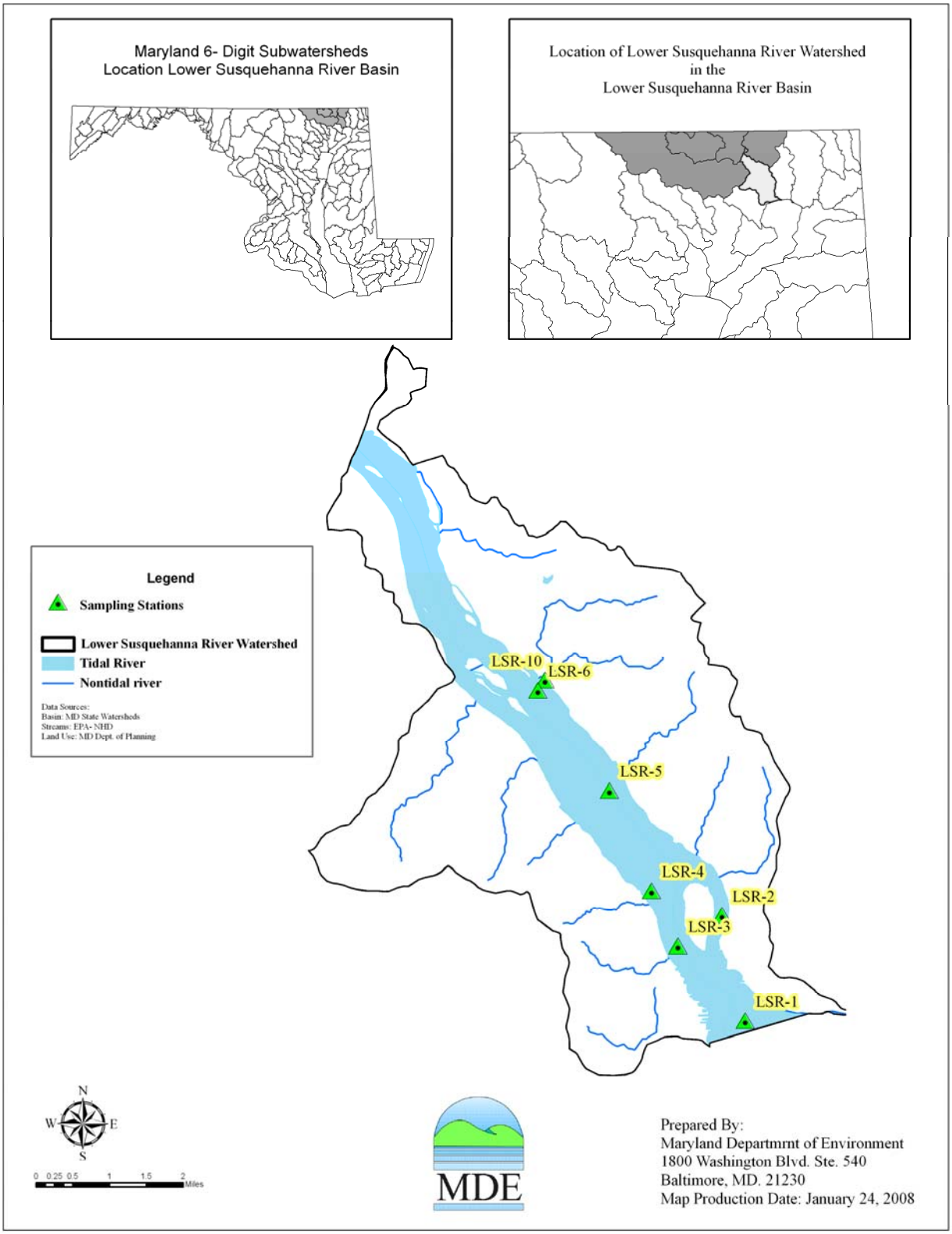


Figure 1: Location Map of the Lower Susquehanna River Drainage Basin

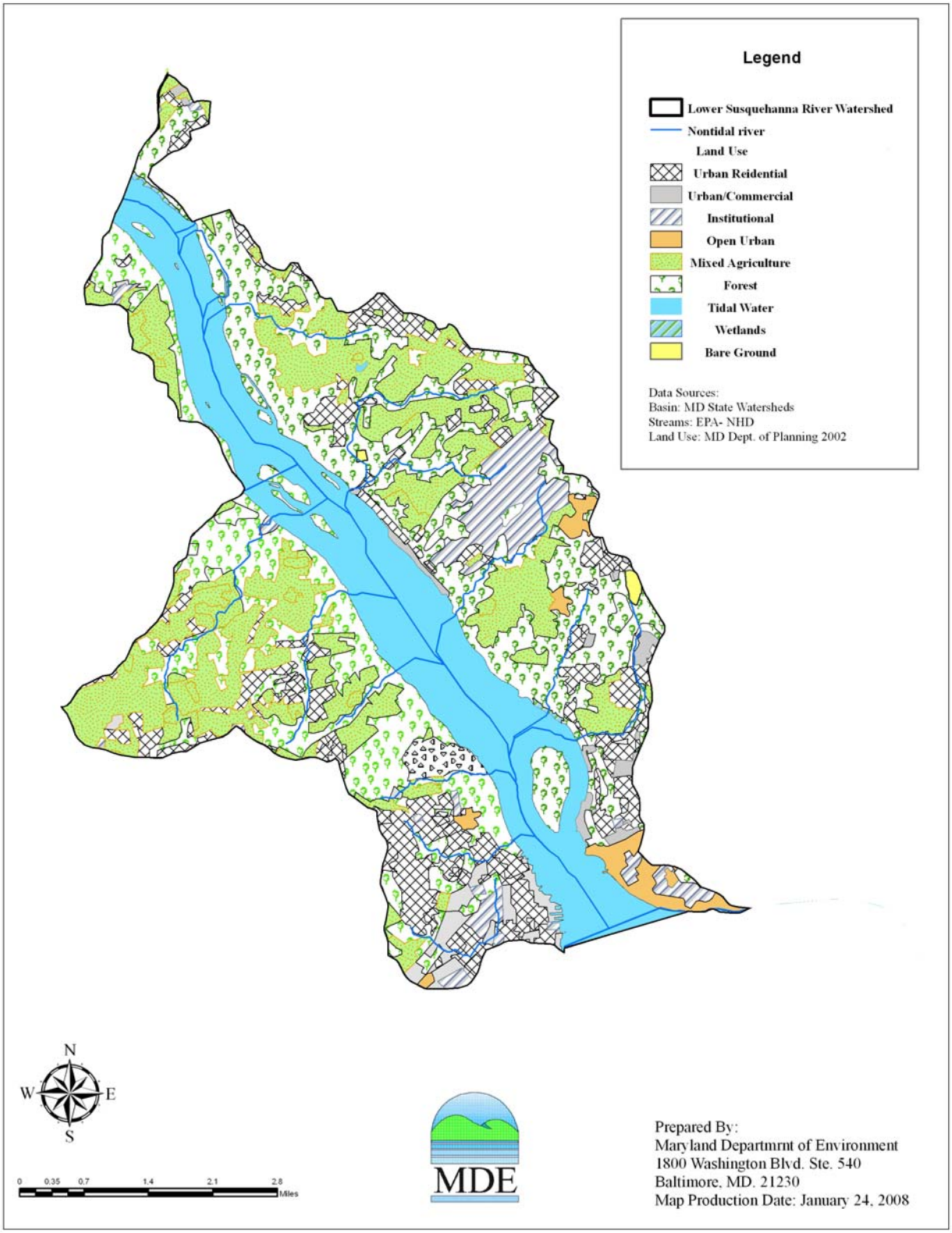


Figure 2: Land Use Map of the Lower Susquehanna River Drainage Basin

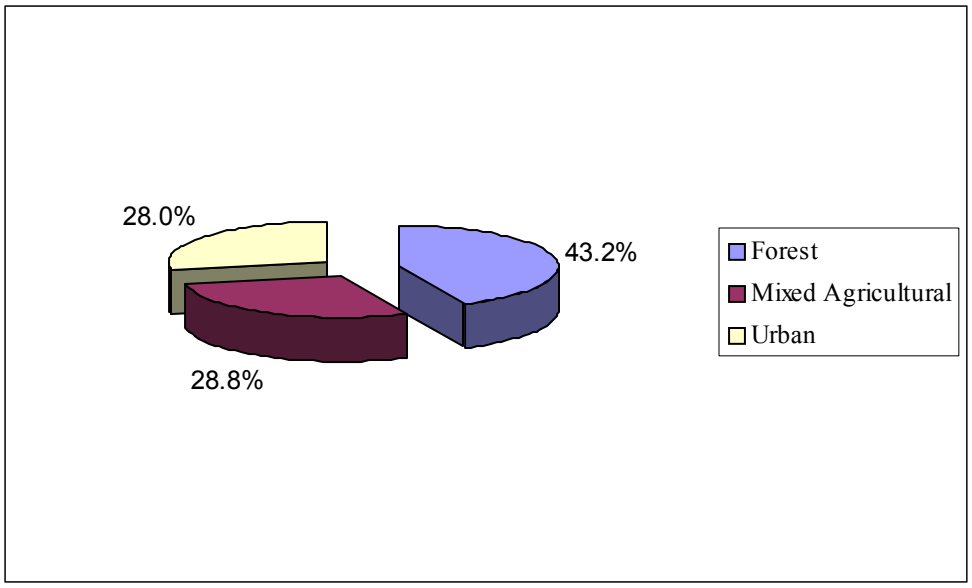


Figure 3: Proportions of Land Use in the Lower Susquehanna River Drainage Basin

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 26.08.02.08B) for the tidal portion of Lower Susquehanna River is Use I-P – water contact recreation, fishing, and protection of aquatic life and wildlife, and public water supply. COMAR 26.08.02.03-1-B(3)(a) defines the Lower Susquehanna River, as a fresh water body. Salinity concentrations for the Lower Susquehanna River are below 1ppt, thus it is a freshwater body and freshwater criterion may be applied. The freshwater aquatic life criteria for Cd are displayed below in Table 1 (COMAR 26.08.02.03-2G).

Table 1: Numeric Water Quality Criteria*

Metal	Fresh Water Aquatic Life Acute Criteria (µg/l)	Fresh Water Aquatic Life Chronic Criteria (µg/l)	Human Health (Water + Organism) (ug/l) (10-5 risk level)

Cd	2.0	0.25	5.0

*Criteria based on default hardness of 100 mg/L

Water column surveys, used to support this WQA, were conducted by University of Maryland Center for Environmental Sciences (UMCES) at seven stations throughout the Lower Susquehanna River from November 2005 to May 2007. The sampling dates were as follows: 11/01/05 (winter dry weather); 6/15/06 (summer dry weather); 5/01/07 (spring wet weather).

Sediment bulk samples were also collected on 6/15/06 at four stations. Sediment samples were analyzed for toxicity using a standard EPA 10 day amphipod test. Table 2 shows the list of stations located in the tidal portion of the Lower Susquehanna with their geographical coordinates. The station locations are presented in Figure 1.

Table 2: Sample Stations for Lower Susquehanna River

Station ID	Latitude	Longitude	Station Description
LSR-1	39.545	-76.076	Mouth of River
LSR-2	39.566	-76.081	T Hatum Mem Bridge East of Garret Island
LSR-3	39.560	-76.093	T Hatum Mem Bridge west of Garret Island
LSR-4	39.571	-76.099	LSR at M E Tydings Mem bridge (I-95)
LSR-5	39.591	-76.110	LSR south of Spencer Island
LSR-6	39.611	-76.128	LSR south of Octarraro Crk discharge
LSR-10	39.613	-76.126	Rock Run (east bank) downstream of confluence with unnamed trib @ intersection of Liberty Grove Rd. and Post Rd.

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

The State uses water hardness adjustment to calculate fresh water aquatic life chronic criteria for those metals (Cd) whose 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. MDE uses an upper limit of 400 mg/l in calculating the hardness adjusted criteria (HAC) when the measured hardness exceeds this value. 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, the Department may perform additional analyses to insure data

quality objectives for the assessments were met. When data is of questionable quality, the Department will take additional samples to establish the validity of the initial assessment. Under circumstances where a water quality criterion exceedance is the result of a hardness adjustment below 25 mg/l, the State will perform a scientific review of the following conditions to determine if the exceedance is valid:

A. Presence/absence of sensitive species in the waterbody of concern.
B. Existence of other environmental conditions (e.g. high Dissolved Organic Carbon (DOC)), which might mitigate the toxicity of metals due to competitive binding/complexation of metals.

This review is necessary because of the scientific uncertainty existing for hardness-toxicity relationships below 25 mg/l due to limited toxicity test data used to develop the relationship.

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

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

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

The HAC parameters for Cd are presented in Table 3 (EPA, 2002).

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

Chemical	Slope (m)	Y Intercept (b)	Conversion Factor (CF)
Cd	0.7409	-4.719	1.101672[(ln hardness)(0.041838)]

3.1 WATER COLUMN EVALUATION

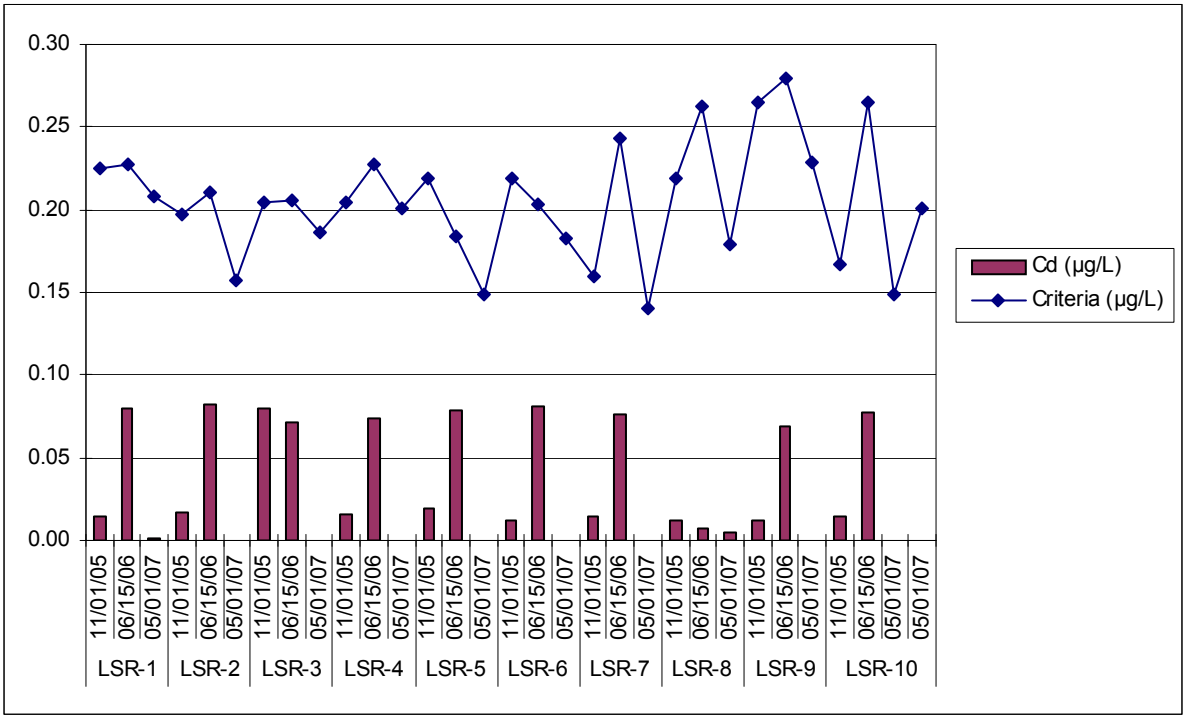
A data solicitation for metals was conducted by MDE, and all readily available data from the past five years was considered in the WQA. The water column data is presented in Table 4 for each station and is evaluated using the fresh water hardness adjusted chronic criteria (Heyes, 2006). Table 4 displays hardness (mg/l), salinity (g/L), detection limit (µg/l), sample concentration (µg/l) and criteria (µg/l) by sampling date. For example, in Table 4 for the sampling date of 11/01/05 at station LSR-1 the hardness is 88.0 mg/l, the hardness-adjusted chronic criterion for Cd is 0.23 µg/l and the Cd sample concentration is 0.01 µg/l. The Cd water column data is also presented in Figure 4.

Table 4: Lower Susquehanna River Water Column Data (Cd)

Station	Hardness (mg/L)	Salinty (g/L)	Date	Detection Limit (µg/L)	Cd (µg/L)	Freshwater Chronic Criteria (µg/L)
LSR-1	88	0.1	11/01/05	0.048	BDL**	0.23
	89	0.1	06/15/06	0.048	0.08	0.23
	78.5	0.1	05/01/07	0.048	BDL**	0.21
LSR-2	73	0.1	11/01/05	0.048	BDL**	0.20
	80	0.1	06/15/06	0.048	0.08	0.21
	52.4	0.1	05/01/07	0.048	BDL**	0.16
LSR-3	77	0.1	11/01/05	0.048	0.08	0.20
	77	0.1	06/15/06	0.048	0.07	0.21
	67.3	0.1	05/01/07	0.048	BDL**	0.19
LSR-4	77	0.1	11/01/05	0.048	BDL**	0.20
	89	0.1	06/15/06	0.048	0.07	0.23
	74.8	0.1	05/01/07	0.048	BDL**	0.20
LSR-5	84	0.1	11/01/05	0.048	BDL**	0.22
	66	0.1	06/15/06	0.048	0.08	0.18
	48.6	0.1	05/01/07	0.048	BDL**	0.15
LSR-6	84	0.1	11/01/05	0.048	BDL**	0.22
	76	0.1	06/15/06	0.048	0.08	0.20
	65.5	0.1	05/01/07	0.048	BDL**	0.18
LSR-10	58		11/01/05	0.048	BDL**	0.17
	111	0.1	06/15/06	0.048	0.08	0.26
	48.6	0.1	05/01/07	0.048	BDL**	0.15
LSR-10 DUP	74.8	0.1	05/01/07	0.048	BDL**	0.20

- Fresh Water Aquatic Life Chronic Criterion (hardness adjusted)
- BDL** - Below detection limit

The range of concentrations for Cd sampled in the field survey is as follows: Cd = BDL to 0.08 µg/l Hardness ranged from 48.6 mg/l to 111 mg/l. The observed concentrations for Cd in the water column were between 2 and 14 times lower than their respective hardness-adjusted freshwater chronic criterion, on average, for each sample.



*All zero values are below the detection limit of 0.048µg/L

Figure 4: Lower Susquehanna River Water Column Data (Cd)

3.2 SEDIMENT QUALITY EVALUATION

To complete the WQA, sediment quality in the Lower Susquehanna River was evaluated using a standard 10-day whole sediment test with the estuarine amphipod *Hyalella azteca* (Fisher, 2007). This species was chosen because of its ecological relevance to the waterbody of concern. *H. azteca* is an EPA-recommended test species for assessing the toxicity of marine and estuarine sediments (EPA, 2001). Four surficial sediment samples were collected on 6/15/06 using a petite ponar dredge (top 2-3 cm) in the Lower Susquehanna River. Control sediments were collected from the Wye River, from a depositional area previously characterized as low in contaminants (Fisher, personal communication). Refer back to Figure 1 for the station locations. Summary of results from the 2006 Metals Monitoring sediment toxicity tests is presented in Table 5. Eight replicates containing ten amphipods each were exposed to the contaminated sediment, as well as control sediment, for testing. Table 5(A) displays average amphipod survival (%) and average amphipod growth (mg dry weight) for *Hyalella azteca* 10 day test.

The test considers three performance criteria: survival, growth rate, and reproduction. For the test to be valid the survival of control sample replicates must be greater than 80%, and there must be a measurable growth rate and reproduction of neonates in the control samples. Survival of amphipods in the field sediment samples was equal or higher than the average survival

demonstrated in the control samples. This comparison was made using Fisher's Least Significance Difference (LSD) test (ά = 0.05). The average survival for control samples in the test was 93.8%. The field sediment sample average survival results were no lower than 95%. No sediment samples in the Lower Susquehanna River exhibited toxicity contributing to mortality.

Similarly, measurable average amphipod reproduction observed in the field sediment samples, which ranged from 0.23 to 0.26 growth for *Hyalella azteca* were equal or higher than the reproduction of 0.20 and 0.23 growth observed in the control samples for the test. This comparison was also made using Fisher's LSD test (ά = 0.05). No sediment sample exhibited toxicity contributing to a lower reproduction.

Table 5: Lower Susquehanna River Sediment Toxicity Test Results

	H. azteca 10-d	
	Survival	Growth
	%	(mg)
Control	93.8	0.2
LSR-1	95	0.23
LSR-2	95	0.23
LSR-3	97.5	0.26
LSR-5	96.3	0.26
Control	93.8	0.23

Table 5(A): Lower Susquehanna River Sediment Toxicity Test Results

Treatment REP	# Surviving amphids	Amphipod (mg)	Amphipod Survival	Amphipod mg. dry wt
Control A	10	0.26	93.8 (7.44)	0.23 (0.024)
Control B	10	0.22		
Control C	9	0.25		
Control D	9	0.22		
Control E	10	0.22		
Control F	10	0.23		
Control G	8	0.22		
Control H	9	0.18		
LSR-1 A	9	0.26	95.0 (5.35)	0.23 (0.042)
LSR-1 B	9	0.23		
LSR-1 C	10	0.25		
LSR-1 D	9	0.26		
LSR-1 E	10	0.24		
LSR-1 F	9	0.13		
LSR-1 G	10	0.24		
LSR-1 H	10	0.24		
LSR-2 A	10	0.24	95.0 (7.56)	0.23 (0.020)
LSR-2 B	10	0.22		
LSR-2 C	10	0.23		
LSR-2 D	10	0.25		
LSR-2 E	10	0.21		
LSR-2 F	9	0.24		
LSR-2 G	9	0.2		
LSR-2 H	8	0.26		
LSR-3 A	10	0.23	97.5 (4.63)	0.26 (0.028)
LSR-3 B	10	0.25		
LSR-3 C	10	0.23		
LSR-3 D	9	0.25		
LSR-3 E	9	0.26		
LSR-3 F	10	0.24		
LSR-3 G	10	0.3		
LSR-3 H	10	0.3		
LSR-5 A	9	0.29	96.3 (5.18)	0.26 (0.014)
LSR-5 B	10	0.26		
LSR-5 C	10	0.26		
LSR-5 D	10	0.24		
LSR-5 E	9	0.26		
LSR-5 F	10	0.27		
LSR-5 G	10	0.26		
LSR-5 H	9	0.26		

4.0 CONCLUSION

The WQA establishes that the water quality standard for Cd is being met in the Lower Susquehanna River watershed. The water column data collected in November 2005, June 2006, and May 2007 at seven monitoring stations (presented in Section 3.1, Table 4) shows that concentrations of Cd in the water column do not exceed the water quality criterion. An ambient sediment bioassay conducted in Lower Susquehanna River, by the University of Maryland Wye Research Center, established that there is no toxicity in the sediment as a result of Cd or other toxics contamination. Therefore, Cd does not impair the water column and sediment in the Lower Susquehanna River. Thus, the designated uses are supported and the water quality standard is being met.

Barring the receipt of contradictory data, this report will be used to support a Cd listing change for Lower Susquehanna River from Category 5 ("water bodies impaired by one or more pollutants 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. Although the waters of Lower Susquehanna River watershed do not display signs of toxic impairments due to Cd, the State reserves the right to require additional pollution controls in the Lower Susquehanna River watershed if evidence suggests that Cd from the basin is contributing to downstream water quality problems.

5.0 REFERENCES

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