Water Quality Analysis of Zinc in Middle Patuxent River, Howard County, Maryland

FINAL

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Table of Contents

List of Figures

List of Tables

List of Abbreviations

ANOVA	Analysis of Variance
COMAR	Code of Maryland Regulations
CWA	Clean Water Act
DNR	Maryland Department of Natural Resources
EPA	Environmental Protection Agency
HAC	Hardness Adjusted Criteria
MDE	Maryland Department of the Environment
MDP	Maryland Department of Planning
mg/l	Milligrams per Liter
NRCS	National Resource Conservation Service
SCS	Soil Conservation Service
SD	Significant Difference
SHA	State Highway Administration
SQG	Sediment Quality Guideline
STATSGO	State Soil Geographic
TMDL	Total Maximum Daily Load
UMCES	University of Maryland Center for Environmental Sciences
UMCFA	University of Maryland Central Farm Area
USGS	United States Geological Survey
WQA	Water Quality Analysis
WQLS	Water Quality Limited Segment
µg/l	Micrograms per Liter
Zn	Zinc

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.

Middle Patuxent River (basin code 02131106), located in Howard County, Maryland, was identified on the State's list of WQLSs as impaired by zinc (Zn) (1996), sediments (1996), nutrients (1996), and impacts to biological communities (2004 listing). The information used for listing Zn 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, which shows that the aquatic life criteria and designated uses associated with Zn are being met in the Middle Patuxent River watershed, and that the 303(d) impairment listings associated with Zn are not supported by the analyses contained herein. The analyses support the conclusion that a TMDL for Zn is not necessary to achieve water quality standards. Barring the receipt of contradictory data, this report will be used to support a Zn listing change for the Middle Patuxent 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 sediments, nutrients, and impacts to biological communities will be addressed separately at a future date.

Although the waters of the Middle Patuxent River watershed do not display signs of toxic impairments due to Zn, the State reserves the right to require additional pollution controls in the Middle Patuxent River watershed if evidence suggests that Zn 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 standards, which result in standards being met; or 4) correction to errors made in the initial listing.

Middle Patuxent River (basin code 02131106) was identified on the State's list of WQLSs as impaired by zinc (Zn) (1996), sediments (1996), nutrients (1996), and impacts to biological communities (2002 listing).

The informational basis (P. Jiapizian, personal communication, 2001) for this listing contended that mean levels of Zn exceeded both the EPA acute and chronic aquatic life criteria for Zn at the time of listing (1996). Although criteria were "exceeded", there were several methodological flaws in the monitoring and listing assessment applied in 1996. First, unfiltered (total metals) samples were compared to dissolved metals criteria. Second, current criteria for Zn 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 half 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 Zn have appropriate detection limits that are well below their respective criteria values.

A Water Quality Analysis (WQA) of Zn for Middle Patuxent River was conducted by MDE using recent water column chemistry data and sediment toxicity data to determine if impairment currently exists. The listings for sediments, nutrients, and impacts to biological communities will be addressed separately at a future date.

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

2.0 GENERAL SETTING

Location

The Middle Patuxent River originates just south of Rt. 144 in the area of Cooksville. The river flows southeast crossing under Rt. 32 and flowing directly through the University of Maryland Central Farm Area (UMFCA). From the UMCFA the river continues south crossing under Rt. 108 and into the Middle Patuxent Environmental Area. Continuing southeast the river crosses under Cedar Lane and Rt. 32 where it defines the northeast property of the Johns Hopkins University Applied Physics Laboratory. The River merges with the Little Patuxent River just south of Interstate 95 near the town of Savage. The location of the watershed is depicted in Figure 1.

Geology/Soils

The Middle Patuxent River watershed is situated within the Northern Piedmont in central Maryland. Sedimentary and igneous rocks that have been metamorphosed characterize the surficial geology of the Northern Piedmont Province. Most of the Northern Piedmont Province is located above the "fall line" on the east coast.

The Middle Patuxent River watershed is comprised of several different soil series including the Chester, Baile, Lehigh, and Beltsville. The Chester series consists of very deep, well-drained soils on upland divides and upper slopes in the Northern Piedmont Province. Saturated hydraulic conductivity is moderately high to high. The Chester soils formed in materials weathered from micaceous schist. The Baile series consists of very deep, poorly drained, moderately low to moderately high saturated hydraulic conductivity, soils on upland depressions and foot slopes. They formed in chiefly mica schist and granitized schist and gneiss. The Lehigh series consists of deep, moderately well and somewhat poorly drained soils formed in residuum from metamorphosed sandstone and shale on hills and low ridges. The Beltsville soil series consist of very deep, moderately well drained soils on uplands and coastal plain landscapes. Saturated Hydraulic Conductivity is high above the fragipan to moderately low or low in the fragipan.

Land use

The land use in the Middle Patuxent River watershed is predominantly agricultural. There are 37,073 total acres in the watershed. Agricultural lands encompass 16,348 acres (44%) in the watershed distributed between cropland, pasture, orchard/horticulture, garden crops, and feed operations. Urban land use comprises 13,000 acres (35%) of the watershed mixed between low density, medium density, high density residential housing, commercial/industrial land use, and open urban land. The watershed contains 7,703 acres (20%) of forested land. Water, and wetlands use 22 acres (<1%) of land. The land use distribution is based on 2002 Maryland Department of Planning (MDP) land use/land cover data. The Middle Patuxent River land use percentages are displayed in Figure 2 and the watershed land use coverage is displayed in Figure 3.

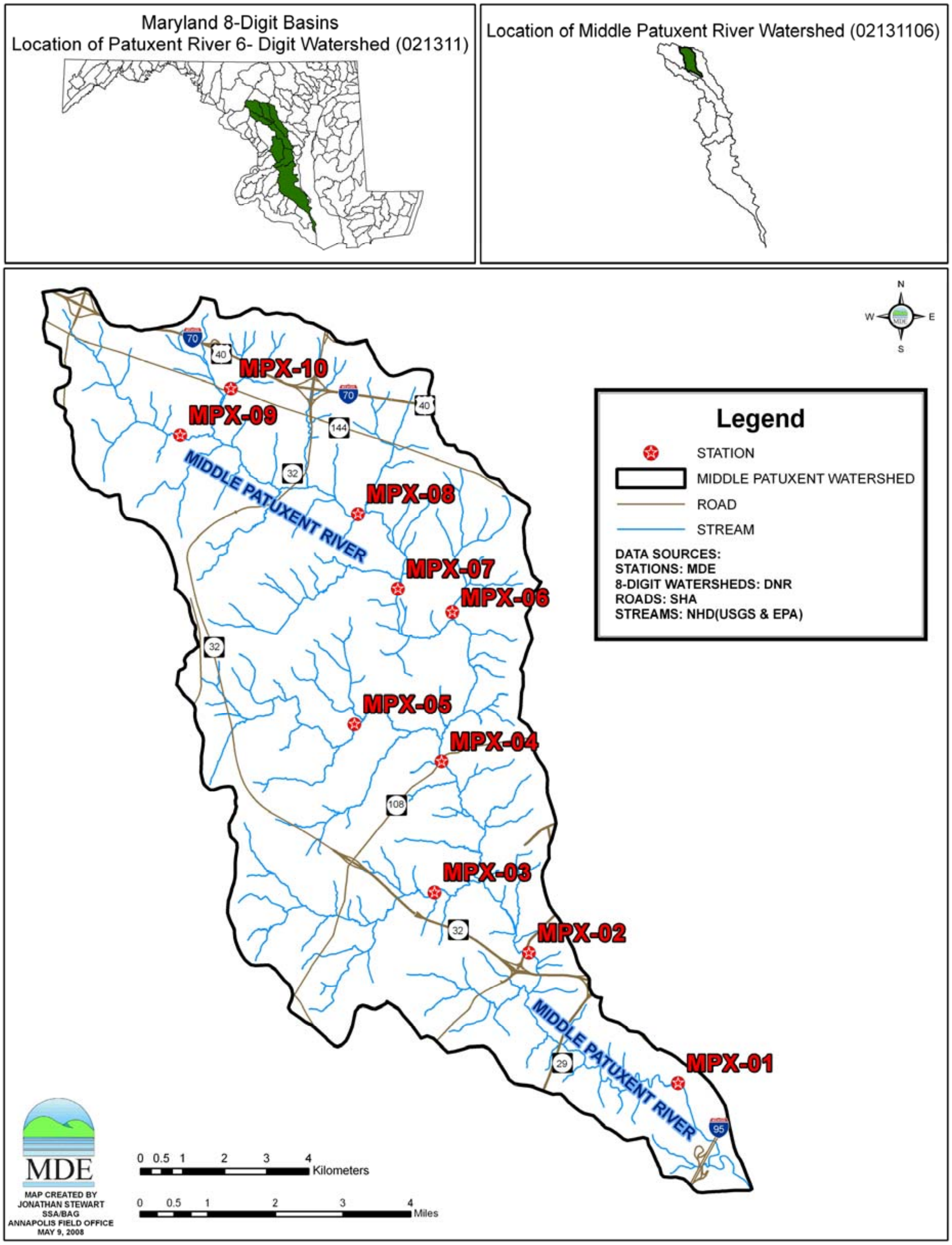

Figure 1: Middle Patuxent Watershed Location Map

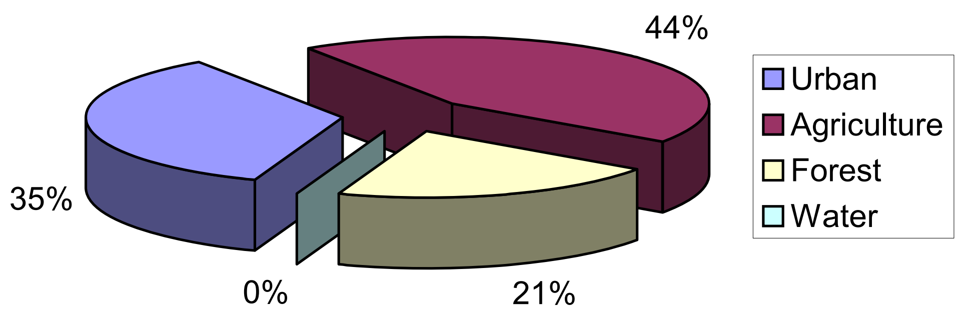

Figure 2: Proportions of Land Use in Middle Patuxent Watershed

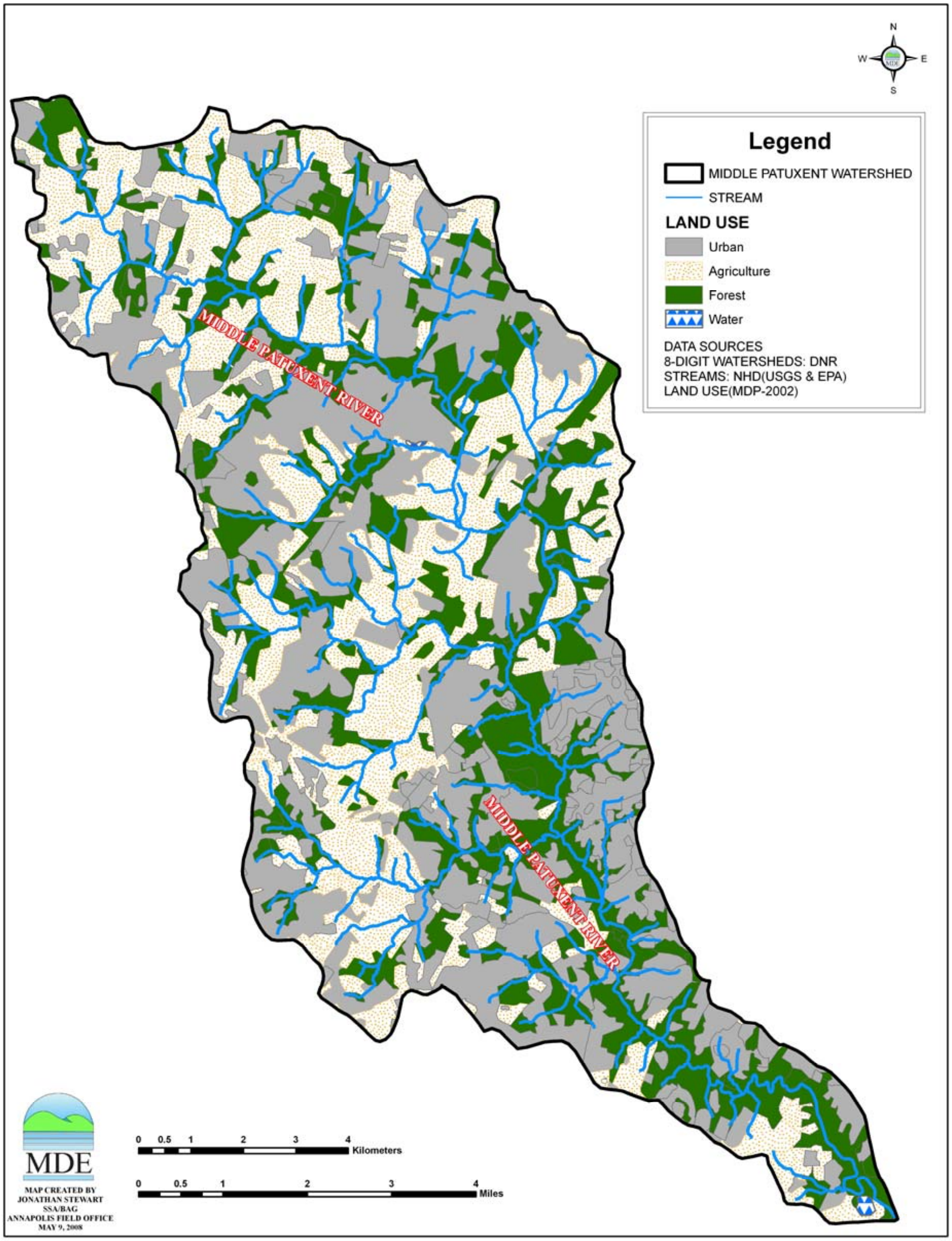

Figure 3: Land Use Map of the Middle Patuxent River Watershed

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 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 for the Middle Patuxent River is Use I-P: *Water Contact Recreation, Protection of Aquatic Life, and Public Water Supply*. (Code of Maryland Regulations (COMAR) 26.08.02.08 (M)(1)(b)). The aquatic life and human health criteria for Zn, which protect these uses, are displayed below in Table 1 (COMAR 26.08.02.03-2G).

Table 1: Numeric Water Quality Criteria

Criteria	Freshwater Aquatic Life* Acute (µg/l)	Freshwater Aquatic Life* Chronic (µg/l)	Human Health (Water + Organism) (µg/l) (10^{-5} risk level)	Human Health (Organism) (µg/l) (10^{-5} risk level)
Zn	120	120	7400	26000

*Aquatic Life Criteria based on default hardness of 100 mg/l

The University of Maryland Center for Environmental Sciences (UMCES-Solomons Island) conducted water column surveys, used to support this WQA, at 10 stations throughout the Middle Patuxent River watershed in November 2005, May 2006, and May 2007. Sediment bulk samples were collected at five stations, MPX-01, MPX-02, MPX-04, MPX-07, and MPX-08 in May 2006. Sediment samples were analyzed for toxicity using a standard EPA freshwater 10-day amphipod test at University of Maryland System – Agricultural Experiment Station (Wye Research and Education Center). Table 2 shows the list of stations with their geographical coordinates (See Figure 1 for locations).

Table 2: Sample Stations for the Middle Patuxent River

Station ID	Latitude	Longitude	Station Description
MPX-1	39.160	76.852	Murray Hill Rd. overpass of Middle Patuxent mainstem
MPX-2	39.188	76.893	Pindell School Rd. overpass of Middle Pax mainstem just north of MD 32 junction
MPX-3	39.201	76.919	MD 32 overpass of Unnamed tributary of Middle Patuxent; 3/4 mile southeast of interchange with MD 108.
MPX-4	39.229	76.917	MD 108 overpass of Middle Patuxent mainstem 0.6 miles northeast of Trotter Rd.
MPX-5	39.237	76.941	0.3 Miles northeast of Sheppard Ln. overpass of unnamed tributary of Middle Patuxent mainstem. Station just downstream of confluence of two unnamed tributaries.
MPX-6	39.261	76.914	Folly Quarter Rd. overpass of unnamed tributary to Middle Patuxent mainstem
MPX-7	39.266	76.929	Carroll Mill Rd. overpass of mainstem Middle Patuxent downstream of Benson Branch
MPX-8	39.282	76.940	Triadelphia Rd. overpass of mainstem Middle Patuxent
MPX-9	39.299	76.989	Pfefferkorn Rd. overpass of mainstem Middle Patuxent
MPX-10	39.309	76.975	Pfefferkorn Rd. at MD 144 (Frederick Rd.) unnamed tributary

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

MDE calculates freshwater 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). 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 are 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 are 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, November 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 chronic HAC parameters for Zn are presented in Table 3 (EPA, November 2002).

Table 3: HAC Parameters (Freshwater Aquatic Life Chronic Criteria)

Chemical	Slope (m)	y Intercept (b)	Conversion Factor (CF)
Zn	0.7409	-4.719	1.102 - ln(hardness)*0.0418

The water column evaluation and sediment quality evaluation are presented in Section 3.1 and 3.2, respectively.

3.1 Water Column Evaluation

MDE conducted a data solicitation for metals and considered all readily available data from the past five years in the WQA. The water column data are presented in Table 5 for each station and evaluated using the freshwater aquatic life chronic criteria (Heyes, 2007). Table 4 displays hardness (mg/l), dissolved Zn sample concentrations (μg/l) and Zn criteria (μg/l). The water column data are also displayed in Figure 4.

Concentrations of Zn in the water column are no greater than 5.09 μg/l. All concentrations are well below their associated freshwater aquatic life hardness adjusted chronic criteria for Zn, while some concentrations are below detection limits. The method detection limit for Zn is shown in Table 4.

Table 4: Metal Detection Limit

Metal	Method Detection Limit (μg/l)
Zn	1.386

Table 5: Middle Patuxent River Water Column Data (Zn)

Station	Date	Hardness (mg/L)	Zn (µg/L)	Zn Criteria* (µg/L)
MPX-1	11/01/05	96	BDL**	114.00
MPX-1	05/30/06	87	5.09	104.99
MPX-1	05/03/07	82.3	BDL**	100.14
MPX-2	11/01/05	92	1.56	110.12
MPX-2	05/30/06	66	2.72	83.08
MPX-2	05/03/07	71.1	BDL**	88.45
MPX-3	11/01/05	100	BDL**	117.85
MPX-3	05/30/06	79	2.30	96.75
MPX-3	05/03/07	82.3	2.40	100.14
MPX-4	11/01/05	96	4.07	114.00
MPX-4	05/30/06	50	BDL**	65.66
MPX-4	05/03/07	67.3	BDL**	84.49
MPX-5	11/01/05	119	BDL**	136.79
MPX-5	05/30/06	77	1.55	94.67
MPX-5	05/03/07	97.2	4.36	115.37
MPX-6	11/01/05	111	2.21	129.28
MPX-6	05/30/06	80	4.57	97.79
MPX-6	05/03/07	82.3	BDL**	100.14
MPX-7	11/01/05	119	BDL**	136.79
MPX-7	05/30/06	70	BDL**	87.33
MPX-7	05/03/07	93.5	2.58	111.60
MPX-8	11/01/05	81	BDL**	98.34
MPX-8	05/30/06	61	1.93	77.71
MPX-8	05/03/07	82.3	BDL**	100.14
MPX-9	11/01/05	65	2.03	82.22
MPX-9	05/03/07	48.6	2.13	64.13
MPX-10	11/01/05	100	2.19	117.85
MPX-10	05/03/07	71.1	2.33	88.45
MPX-10 DUP	05/03/07	63.6	4.29	80.49

*Freshwater Aquatic Life Hardness Adjusted Chronic Criterion

**Below Detection Limit

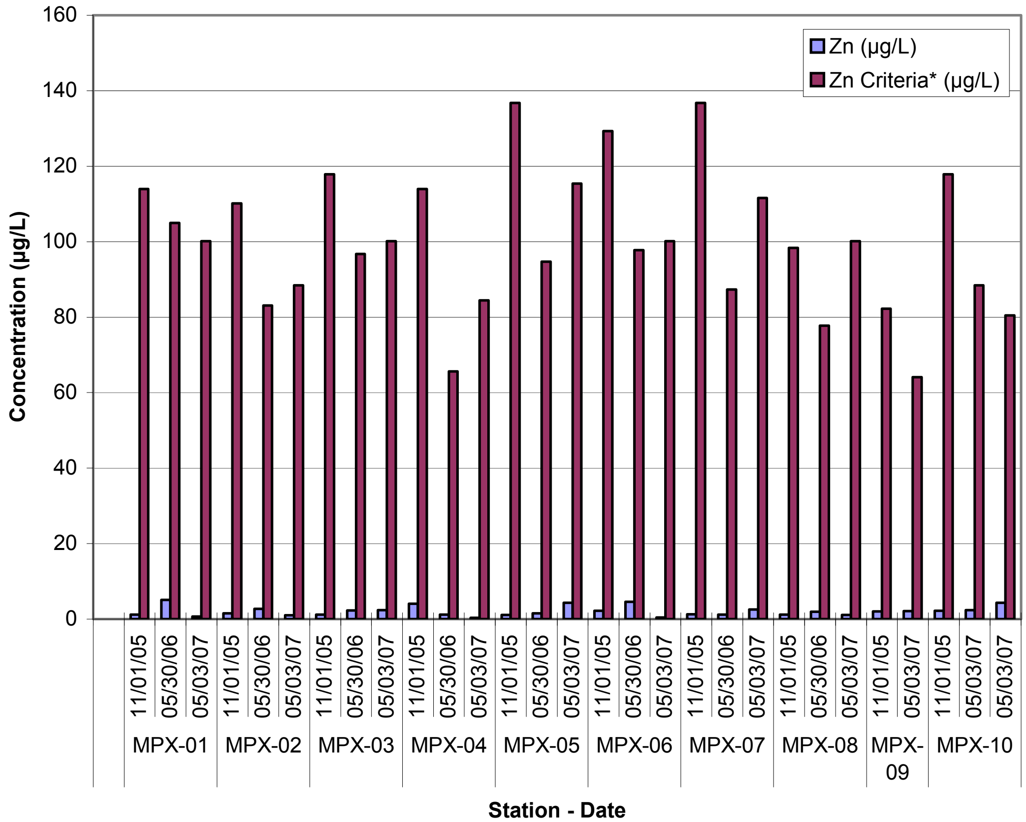

Figure 4: Middle Patuxent River Water Column Data (Zn)

3.2 Sediment Quality Evaluation

Sediment quality in the Middle Patuxent River watershed was evaluated using a 10-day whole sediment test with the freshwater amphipod *Hyalella azteca* (Fisher, 2007*)*. 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, 2000). Five surficial sediment samples were collected in May 2006 using a petite ponar dredge (top 2 cm) in the Middle Patuxent River watershed. Control sediments were collected from Bigwood Cove, Wye River, from a depositional area previously characterized as low in contaminants (Fisher, 2007). Refer to Figure 1 for the station locations. The results are presented in Table 6. Eight replicates containing ten amphipods each were exposed to the contaminated sediment samples, as well as a control sediment sample, for testing. The table displays average amphipod survival (%) and average amphipod growth (mg dry weight).

Table 6: Middle Patuxent River Sediment Toxicity Test Results

Treatment REP	Amphipod Survival (#)	Amphiopod Weight (mg)	Treatment % Survival (SD)	Treatment mg. dry wt. (SD)
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		
MPX-1 A	9	0.26	93.8 (7.44)	0.27 (0.035)
MPX-1 B	9	0.26		
MPX-1 C	10	0.25		
MPX-1 D	10	0.23		
MPX-1 E	9	0.32		
MPX-1 F	10	0.26		
MPX-1 G	8	0.33		
MPX-1 H	10	0.28		
MPX-2 A	10	0.26	97.5 (4.63)	0.24 (0.042)
MPX-2 B	10	0.27		
MPX-2 C	10	0.3		
MPX-2 D	9	0.26		
MPX-2 E	10	0.22		
MPX-2 F	10	0.23		
MPX-2 G	10	0.16		
MPX-2 H	9	0.24		
MPX-4 A	10	0.24	97.5 (4.63)	0.23 (0.030)
MPX-4 B	10	0.2		
MPX-4 C	9	0.23		
MPX-4 D	10	0.22		
MPX-4 E	9	0.18		
MPX-4 F	10	0.26		
MPX-4 G	10	0.27		
MPX-4 H	10	0.24		

Table 6: Middle Patuxent River Sediment Toxicity Test Results (Cont'd)

Treatment REP	Amphipod Survival (#)	Amphiopod Weight (mg)	Treatment % Survival (SD)	Treatment mg. dry wt. (SD)
MPX-7 A	9	0.21	93.8 (7.44)	0.24 (0.031)
MPX-7 B	9	0.19		
MPX-7 C	8	0.24		
MPX-7 D	9	0.23		
MPX-7 E	10	0.29		
MPX-7 F	10	0.26		
MPX-7 G	10	0.24		
MPX-7 H	10	0.26		
MPX-8 A	9	0.2	95.0 (5.35)	0.24 (0.044)
MPX-8 B	9	0.24		
MPX-8 C	10	0.32		
MPX-8 D	10	0.2		
MPX-8 E	10	0.2		
MPX-8 F	9	0.27		
MPX-8 G	9	0.28		
MPX-8 H	10	0.24		

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

Survival of amphipods in the field sediment samples was the same or greater than the average survival demonstrated in the control sediment sample. The average survival for the control sediment sample was 93.8%. The average survival for all field sediment samples ranged between 93.8% and 97.5%. The control sediment sample exhibited an average final dry weight of 0.23 mg, in contrast to a range of 0.23 mg to 0.27 mg average final dry weight for field sediment samples. Thus, the sediment samples in the Middle Patuxent River were found not to be toxic.

4.0 CONCLUSION

The WQA establishes that the water quality standard for Zn is being met in the Middle Patuxent River watershed. The water column data collected in November 2005, May 2006, and May 2007 at ten monitoring stations (presented in Section 3.1, Table 4) shows that concentrations of Zn in the water column do not exceed the water quality criterion. An ambient sediment bioassay conducted in the Middle Patuxent River, by the University of Maryland Wye Research Center, established that there is no toxicity in the sediment as a result of Zn or other toxics contamination. Therefore, Zn does not impair the water column and sediment in the Middle Patuxent 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 Zn listing change for the Middle Patuxent 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 MDE proposes the revision of Maryland's 303(d) list for public review in the future. Although the waters of the Middle Patuxent River watershed do not display signs of toxic impairments due to Zn, the State reserves the right to require additional pollution controls in the Middle Patuxent River watershed if evidence suggests that Zn from the basin is contributing to downstream water quality problems.

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