# Water Quality Analysis of Heavy Metals for the Lower North Branch Patapsco River in Baltimore, Carroll, Howard and Anne Arundel Counties and Baltimore City, Maryland

# **FINAL**

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## List of Abbreviations

As Arsenic
Be Beryllium
Cd Cadmium

COMAR Code of Maryland Regulations

Cr Chromium
Cu Copper

CWA Clean Water Act

DOC Dissolved Organic Carbon

DNR Department of Natural Resources EPA Environmental Protection Agency

HAC Hardness-adjusted Criteria

Hg Mercury

IBI Index of Biotic Integrity

MBSS Maryland Biological Stream Survey

MDE Maryland Department of the Environment

mg/l Milligrams per Liter mg/kg Milligrams per Kilogram

Ni Nickel

NPDES National Pollution Discharge Elimination System

Pb Lead

ppb Parts per billion Sb Antimony

SCS Soil Conservation Service

Se Selenium

SSURGO Soil Survey Geographic
TMDL Total Maximum Daily Load
USGS United States Geological Survey

WER Water Effects Ratio 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. 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 Lower North Branch Patapsco River (basin code 02-13-09-06), located in Baltimore, Howard, Anne Arundel Counties and Baltimore City, was identified on the State's list of WQLSs as impaired by heavy metals (1996 listing), nutrients (1996 listing), suspended sediments (1996 listing), fecal coliform (2002 listing) and evidence of biological impacts (2002 listing). All impairments are listed for the non-tidal streams. This report provides an analysis of recent heavy metals monitoring data, including hardness data. A data solicitation for heavy metals was conducted by MDE and all readily available data from the past five years was considered. The study finds that the applicable aquatic life criteria for heavy metals and the designated uses supported by those criteria are being met in the Lower North Branch Patapsco River except for Herbert Run where a single exceedance of copper was found. Therefore a TMDL for heavy metals is not required for the 8-digit basin, but a TMDL for Cu may be needed in Herbert Run, a tributary of the main branch in the lower most 12-digit basin (basin code 02-13-09-06-10-12). Based on impairment listing methodologies applied by the Maryland Department of the Environment (MDE) further investigation is necessary to determine if Herbert Run is impaired for Cu. Only one exceedance of Cu was found in six samples, which is insufficient to justify a finding of impairment. Additional monitoring is necessary to establish whether the exceedance was the result of a single anomalous event or further exceedances will reoccur resulting in an impairment. Barring the receipt of any contradictory data, this report will be used to support the removal of the Lower North Branch Patapsco River from Maryland's list of WQLSs for heavy metals when the Maryland Department of the Environment (MDE) proposes the revision of Maryland's 303(d) list for public review in the future. Herbert Run will remain on Part 3 (waterbodies that have insufficient data to define the impairment status) of the 303(d) list with Cu as the impairing substance. The nutrient, suspended sediment, fecal coliform and biological impairments will be addressed at a future date.

Although the waters of the Lower North Branch Patapsco River except for Herbert Run do not display signs of toxic impairments due to heavy metals exceeding water quality criteria, the State reserves the right to require additional pollution controls in the Lower North Branch Patapsco River watershed if evidence suggests that heavy metals from the basin are 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) of the specified substance that the waterbody can receive without violating water quality standards, or demonstrate that water quality standards are being met.

A segment identified as a WQLS may not require the development and implementation of a TMDL if current information contradicts the previous finding of an impairment. The most common factual scenarios obviating the need for a TMDL are as follows: 1) more recent data indicating that the impairment no longer exists (i.e., water quality criteria are being met); 2) more recent and updated water quality modeling demonstrates that the segment is now attaining 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.

The Lower North Branch Patapsco River (basin code 02-13-09-06) was first identified on the 1996 303(d) list submitted to EPA by the Maryland Department of the Environment (MDE) as impaired by heavy metals, nutrients and suspended sediments, with fecal coliform and evidence of biological impacts added to the list in 2002. All impairments are listed for the non-tidal streams. The initial listing for heavy metals is questionable because: 1) the listing was based on total recoverable metals (current standard is based on dissolved metals); 2) inappropriate sampling techniques were applied (lack of filtration); 3) supporting hardness data needed to interpret criteria was not available; and 4) a default hardness of 100 mg/L was used to convert and relate the total recoverable metals to the dissolved criteria, which superceded the total recoverable metals criteria.

A water quality analysis (WQA) of heavy metals for Lower North Branch Patapsco River was performed using recent water column data. A data solicitation for heavy metals data was conducted by MDE and all readily available data from the past five years was considered. The study finds that the applicable aquatic life criteria for heavy metals and the designated uses supported by those criteria are being met in the Lower North Branch Patapsco River except for Herbert Run where a single exceedance of copper was found. Therefore a TMDL for heavy metals is not required for the 8-digit basin, but a TMDL for Cu may be needed in Herbert Run, a tributary of the main branch in the lower most 12-digit basin (basin code 02-13-09-06-10-12). Based on impairment listing methodologies applied by the Maryland Department of the Environment (MDE) further investigation is necessary to determine if Herbert Run is impaired for Cu. Only one exceedance of Cu was found in six samples, which is insufficient to justify an impairment. Additional monitoring is necessary to establish whether the exceedance was the result of a single anomalous event or further exceedances will occur resulting in impairment. Barring the receipt of any contradictory data, this report will be used to support the removal of the Lower North Branch Patapsco River from Maryland's list of WQLSs for heavy metals when the Maryland Department of the Environment (MDE) proposes the revision of Maryland's

303(d) list for public review in the future. Herbert Run will remain on Part 3 (waterbodies that have insufficient data to define the impairment status) of the 303(d) list with Cu as the impairing substance. The nutrient, suspended sediment, fecal coliform and biological impairments will be addressed at a future date.

The term "heavy metals" and "metals" are interchangeable and generally interpreted to include those metallic elements from periodic table groups IIA through VIA. At trace levels, many of these elements are necessary to support life. However, at elevated levels they become toxic, may build up in biological systems, and become a significant detriment to aquatic life. For the purposes of this WQA, metals are those priority pollutant metals that are commonly regulated in National Pollution Discharge Elimination System (NPDES) industrial or NPDES stormwater discharges. The following metals were sampled in the Lower North Branch Patapsco River: arsenic (As); cadmium (Cd); chromium (Cr); copper (Cu); mercury (Hg); nickel (Ni); lead (Pb); selenium (Se) and zinc (Zn).

Basin geological conditions, land use, and past/present industrial practices did not indicate the potential for the presence of other priority pollutants, such as antimony (Sb) and beryllium (Be) - metals commonly found at Superfund sites. If a specific water quality impairment exists that identifies specific metal(s) as impairing substances, sampling and analysis may be limited to those metal(s) of concern.

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

## 2.0 GENERAL SETTING

The Lower North Branch Patapsco River watershed is located in the Patapsco River region of the Chesapeake Bay watershed within Maryland (see Figure 1). The watershed covers a portion of Baltimore, Howard and Anne Arundel County and Baltimore City. The watershed area covers 75,756 acres.

The Lower North Branch Patapsco River watershed lies within the Piedmont and Coastal Plain provinces of 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 stream bed. These crystalline formations decrease in elevation from northwest to southeast and eventually extend beneath the younger sediments of the Coastal Plain. The fall line represents the transition between the Atlantic Coastal Plain Province and the Piedmont Province. The Atlantic Coastal Plain surficial geology is characterized by thick, unconsolidated marine sediments deposited over the crystalline rock of the piedmont province. The deposits include clays, silts, sands and gravels (Coastal Environmental Services, 1995).

The Lower North Branch Patapsco River watershed drains from northwest to southeast, following the dip of the underlying crystalline bedrock in the Piedmont Province. The surface

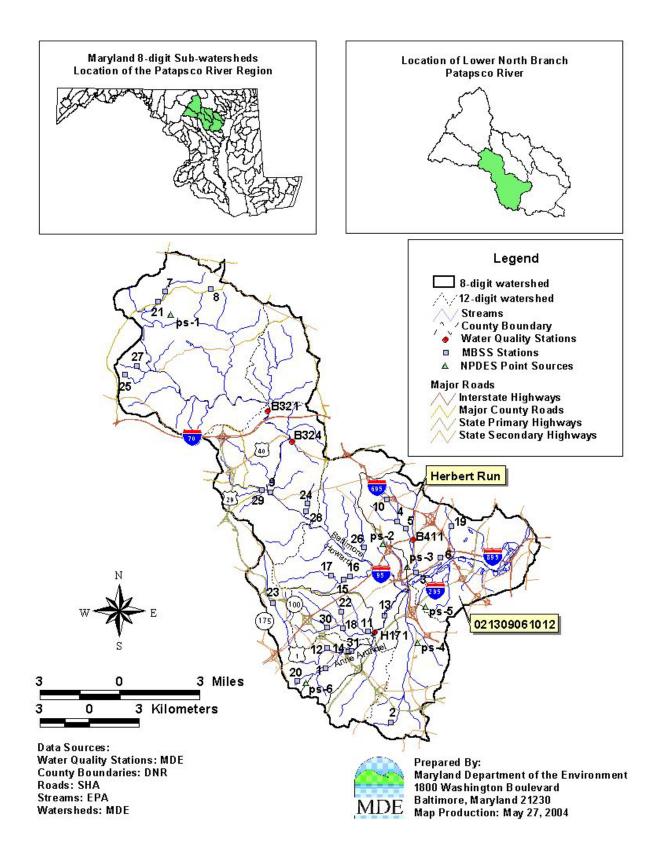


Figure 1: Watershed Map of the Lower North Branch Patapsco River

elevations range from approximately 620 feet to sea level at the Chesapeake Bay shorelines. Stream channels of the sub-watersheds are well incised in the Eastern Piedmont, and exhibit relatively straight reaches and sharp bends, reflecting their tendency to following zones of fractured or weathered rock. The stream channels broaden abruptly as they flow down across the fall line into the soft, flat Coastal Plain sediments (Coastal Environmental Services, 1995).

The watershed is comprised primarily of B and C type soils. Soil type is categorized by four hydrologic soil groups developed by the Soil Conservation Service (SCS). The definitions of the groups are as follows (SCS, 1976):

Group A: Soils with high infiltration rates, typically deep well-drained to excessively drained sands or gravels.

Group B: Soils with moderate infiltration rates, generally moderately deep to deep, moderately well to well drained soils with moderately fine to moderately coarse textures.

Group C: Soils with slow infiltration rates, mainly soils with a layer that impedes downward water movement or soils with moderately fine to fine texture.

Group D: Soils with very slow infiltration rates, mainly clay soils, soils with a permanently high water table, and shallow soils over nearly impervious material.

The soil distribution within the watershed is approximately 5.1% soil group A, 41.8% soil group B, 40.9% soil group C and 12.2% soil group D. Soil data was obtained from Soil Survey Geographic (SSURGO) coverages created by the National Resources Conservation Service.

The Lower North Branch Patapsco River watershed contains mostly urban and forest land use (see Figure 2). No major point sources discharge metals within the watershed. Six minor facilities are regulated for various metals and are listed in Table 1. The location of these facilities is displayed in Figure 1. The land use distribution in the watershed is approximately 39.2% forest/herbaceous, 49.62% urban, 10.18% agricultural and 1% water (Maryland Department of Planning, 2002).

**Table 1: Lower North Branch Patapsco River Point Source Facilities** 

Station	NPDES	Facility	Latitude	Longitude	Metals
ps-1	MD0063924	Hernwood Landfill- North Site	39.362	-76.861	Pb, Zn
ps-2	MD0057991	UMBC Technology Center	39.238	-76.714	Cu
ps-3	MD0001813	Diageo North America Inc.	39.225	-76.697	Cu
ps-4	MD0000868	Northrop Grumman Corp-BWI	39.184	-76.690	Cu
ps-5	MD0000850	Northrop Grumman Corp-ATC	39.204	-76.685	Cu
ps-6	MD0059374	Baltimore Airoil Company	39.163	-76.768	Cr, Cu, Ni, Zn

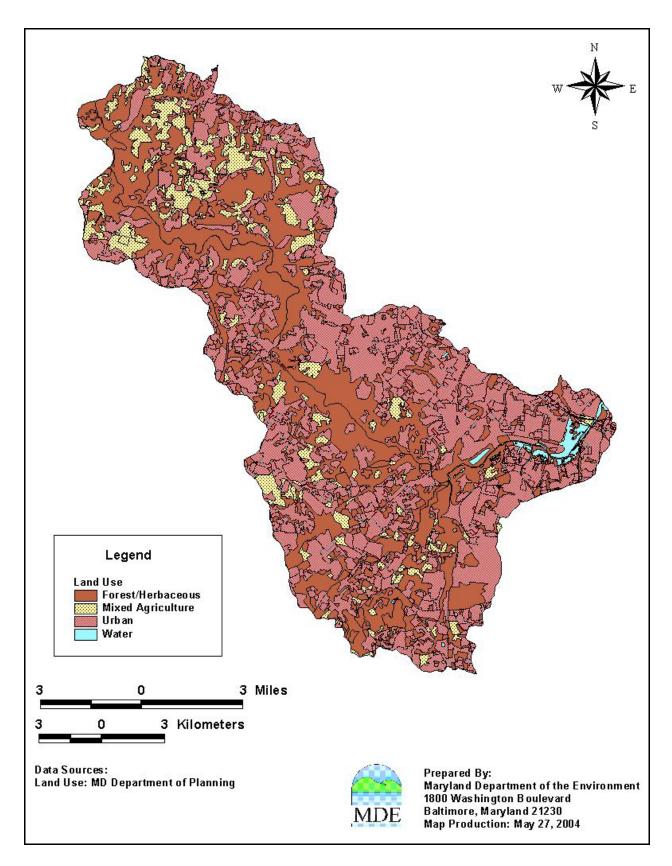


Figure 2: Land Use Map of Lower North Branch Patapsco River Watershed

# 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 the designated use 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. The water quality standard is only applicable to the water column, therefore, MDE has also evaluated sediment quality, mercury in fish tissue and biological conditions of the watershed.

The Maryland Surface Water Use Designation (Code of Maryland Regulations (COMAR) 26.08.02.08J) for the Lower North Branch Patapsco River is Use I – *water contact recreation*, *fishing, and protection of aquatic life and wildlife*. The applicable numeric aquatic life criteria and human health criteria (fish consumption) for dissolved metals in freshwater are described below in Table 2 (COMAR 26.08.02.03-2G). There are two species of chromium, trivalent Cr (III) and hexavalent Cr (VI). Cr (VI) has the highest toxicity of the Cr species, therefore, the numeric criterion is more stringent. Total chromium concentrations were analyzed in the water column survey and are compared with the Cr (VI) numeric water quality criterion.

Metal	Fresh Water Aquatic Life Acute Criteria (µg/I) *	Fresh Water Aquatic Life Chronic Criteria (μg/l) *	Human Health Criteria Fish Consumption (μg/l)		
As	340	150	41		
Cd	4.3	2.2	-		
Cr (VI)	16	11	-		
Cu	13	9	1,300		
Hg	1.4	0.77	0.051		
Ni	470	52	4,600		
Pb	65	2.5	-		
Se	20	5	11000		
Zn	120	120	69,000		

**Table 2: Numeric Water Quality Criteria (Metals)** 

MDE considered information regarding mercury (Hg) in fish tissue for this water quality analysis. In a study conducted by MDE, fifteen fish tissue samples of varying species were collected and analyzed for mercury concentrations at one station in the Lower North Branch Patapsco River in October 1992 and 1995 (MDE, 2000). The average mercury concentration was  $76.3 \mu g/kg$  (wet weight). This compares to the EPA fish tissue residue criterion of 300

<sup>\*</sup> Assumes hardness of 100 mg/L

 $\mu g/kg$  (EPA, 2001), indicating that a low potential exists for excessive mercury bioaccumulation in fish species residing in this basin.

This water quality assessment also considered the potential impact of metals on indices of biological integrity (IBI). Maryland Biological Stream Survey (MBSS) data was collected at seventeen stations in 1995-1996 and fourteen stations in 2002 throughout the watershed. Refer to Figure 1 for station locations. The MBSS data is presented in Table 3 (Maryland Department of Natural Resources, 2004).

Table 3: Lower North Branch Patapsco River MBSS Data

Station	Sample Year	Fish IBI	Benthic IBI	Physical Habitat Index	Channel Alteration	Bank Stability
1	1995	4.25	3.86	84.18	11	10
2	1995	3.25	2.71	13.15	4	16
3	1995	3.75	1.57	83.73	5	5
4	1995	2.33	3	66.12	10	7
5	1995	1.67	1.57	63.36	2	16
6	1996	1	1	20.81	7	5
7	1995	3.67	4.33	66.14	16	15
8	1995	1	3.67	18.84	7	6
9	1995	1	2.11	67.95	15	16
10	1995	1	1.89	60.93	9	5
11	1995	4.5	1.57	85.31	12	10
12	1995	3.44	1.57	88.78	11	5
13	1996	3.25	2.71	46.62	5	4
14	1995	4.25	2.43	69.25	6	7
15	1995	3.44	3.67	65.21	13	11
16	1996	3.67	1	60.44	13	10
17	1995	3.89	3.44	40.74	10	8
18	2000	3.67	3	ı	1	-
19	2000	1.67	2.56	ı	1	-
20	2000	ı	3	ı	1	-
21	2000	2.56	3.22	ı	1	-
22	2000	ı	2.56	ı	ı	-
23	2000	3.22	3.67	ı	1	-
24	2000	1.22	2.56	ı	1	-
25	2000	1	2.78	ı	1	-
26	2000	1.22	2.33	1	ı	-
27	2000	-	3.67	-	-	-
28	2000	1.22	1.89	-	-	-
29	2000	3	3.44	1	ı	-
30	2000	4.11	3.67	-	-	-
31	2000	4.56	1.89	-	-	-

The average value for fish IBI was 3.02 in 1995-1996 and 2.65 in 2002 and the average value for benthic IBI was 2.48 in 1995-1996 and 2.87 in 2002. The acceptable threshold for fish and benthic IBI is 3.0 or above. These data confirm the 2002 listing for biological impacts. The average physical habitat index for the 1995-1996 MBSS sampling was 58.9 out of 100. A rating of 72 or above is considered good. The channel alteration and bank stability average values for the 1995-1996 MBSS sampling were 9.2 and 9.2 (out of 20), respectively. Bank instability and channel alteration is significant for values less than 10. An additional Patapsco River Basin stream assessment study conducted by DNR establishes that over 65 % of the stream miles in the basin have degraded bank conditions in terms of unstable or moderately unstable stream banks (Boward, 1998). This information suggests that degraded physical habitat is a major contributing factor to the depressed fish and benthic IBI.

Sediment quality could not be assessed in this WQA due to the lack of depositional areas in the Lower North Branch Patapsco River watershed. Field sampling teams observed no appreciable sediment in the streambed; as a result they were unable to collect samples. The Lower North Branch Patapsco River is classified as a high gradient stream; therefore, sediment entering the channel tends to be flushed out leaving no appreciable deposition of fine grained material. Coarse grained material generally does not accumulate toxic substances. There are also no known sources of contaminated soil in the watershed thus any eroded sediment shall be clean, containing only trace amounts of metals. Furthermore, the metals concentrations within the water column are extremely low except for the observed criterion exceedance of Cu in Herbert Run. Based on the weight of this evidence, it is unlikely that metals have an impact on biological integrity in the water column or sediment except possibly in Herbert Run.

Water column surveys conducted at four monitoring stations in the Lower North Branch Patapsco River from May 2001 to April 2002 were used to support this WQA. For every sample, dissolved concentrations of the nine metals were determined. Table 4 shows the list of stations with their geographical coordinates and descriptive location in the Lower North Branch Patapsco River. Refer back to Figure 1 for station locations.

Table 4: Water Quality Analysis Stations for Lower North Branch Patapsco River

Station I.D.	GPS coordinates	Station Description						
B321	39.310	Patapsco River at Hollofield, MD						
76.793		T atapaco Tiver at Hollolleid, MD						
B324	39.294	Miller Run						
D324	76.776	Willer Pari						
B411	39.240	East Branch Herbert Run at Arbutus, MD						
D411	76.693	Last Bianch Heibert Run at Albutus, MD						
H171	39.190	Deep Run						
''''	76.720	Deep Ruit						

Water column sampling was performed six times at stations B321, B324 and B411 and five times at station H171 from May 2001 to April 2002 to capture seasonal variations. The sampling dates were as follows: May 21, 2001 (spring wet weather); June 11, 2001 (spring dry weather);

July 25, 2001 (summer dry weather); July 30, 2001 (summer wet weather); April 3, 2002 (spring dry weather) and April 25, 2002 (spring wet weather).

For the water quality evaluation, a comparison is made between the Cu and Pb water column concentrations and the hardness-adjusted fresh water aquatic life chronic criteria, the most stringent of the numeric water quality criteria. Simultaneous hardness concentrations were obtained for each station to adjust the fresh water aquatic life chronic criteria that are established at a hardness of 100 mg/l for Cu and Pb.

The State uses hardness adjustment to calculate fresh water aquatic life chronic criteria for those metals (Cd, Cu, Pb, Zn and Ni) for which toxicity is a function of total hardness. The fresh water aquatic life chronic criteria are not adjusted for Cr (VI), Se and Hg because hardness either does not affect the bioavailability of these metals to aquatic life or there is significant uncertainty in the correlation between hardness and criteria. According to EPA's National Recommended Water Quality Criteria (EPA, Nov 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 criteria (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 veracity 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.

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The HAC equation for Cu and Pb is as follows (EPA, 2002):

```
\begin{split} HAC &= e^{(m[\ln{(Hardness(mg/l)]+b)}} * CF \\ Where, \\ HAC &= Hardness-adjusted Criterion (\mu g/l) \\ m &= slope \\ b &= y intercept \\ CF &= Conversion Factor (conversion from totals to dissolved numeric criteria) \end{split}
```

The HAC parameters for metals are presented in Table 5 (EPA, 2002).

**Table 5: HAC Parameters (Fresh Water Aquatic Life Chronic Criteria)** 

Chemical	Slope (m)	lope (m) y Intercept (b) Conversion Fact				
Cd	0.7409	-4.719	1.102 - In(hardness)*0.0418			
Cu	0.8545	-1.702	0.960			
Pb	1.2730	-4.705	1.462 - In(hardness)*0.146			
Ni	0.8460	0.0584	0.997			
Zn	0.8473	0.884	0.986			

In instances where hardness data is not available, the State will calculate an average of existing hardness concentrations for each station. In applying average hardness, the sampling date for which hardness data is unavailable must not fall during a rainfall event substantially greater than the remaining sampling dates used to calculate the average. A major rainfall event has the potential to reduce hardness. An analysis of rainfall data from the National Weather Service (NWS) precipitation gauge (0180465) at Baltimore/Washington International Airport (BWI) shows no significant variation in storm events for the sampling dates, thus the average will apply. This is the closest gauge to Lower North Branch Patapsco River and is likely to be representative of the rainfall events that occur within the watershed.

## 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 7 through Table 10 for each station and is evaluated using the fresh water aquatic life chronic HAC, the more stringent of the numeric water quality criteria for metals (Baker, 2002). Each table displays hardness (mg/l), sample concentrations ( $\mu$ g/l) and fresh water chronic HAC ( $\mu$ g/l) by sampling date. For example, in Table 7 for the sampling date of 6/11/01 the hardness is 26.5 mg/l, the hardness-adjusted criterion for Cu is 2.88  $\mu$ g/l and the Cu sample concentration is 0.91  $\mu$ g/l. The hardness concentrations reported in bold are for sampling dates in which hardness was not measured and an average value was applied. The detection limits for metals analysis are displayed in Table 6. The water quality data for all stations is also displayed in Figure 3 and Figure 4 for Cu and Pb, respectively.

**Table 6: Metals Analysis Detection Limits** 

Analyte	Detection Limit (μg/l)
As	0.09
Cd	0.001
Cr	0.03
Cu	0.01
Hg	0.00004
Ni	0.01
Pb	0.003
Se	0.09
Zn	0.25

Table 7: Station B321 (Patapsco River at Hollofield) Water Column Data

Sampling Date	5/2	5/21/01 6/11/		1/01	7/25/01		7/30/01		4/3/02		4/25/02		
Hardness (mg/l)	31	1.2	26	6.5	33	33.2		30.6		32.9		33.2	
Analyte	Sample (µg/l)	Criteria* (µg/l)											
As	ND	41	0.11	41	0.28	41	0.28	41	0.22	41	0.08	41	
Cd	ND	0.95	ND	0.84	0.02	0.99	0.01	0.93	0.01	0.98	0.01	0.99	
Cr	ND	11	0.32	11	0.36	11	0.11	11	0.17	11	0.09	11	
Cu	ND	3.31	0.91	2.88	1.28	3.49	1.05	3.26	0.89	3.46	1.12	3.49	
Hg	ND	0.051	0.0005	0.051	0.0006	0.051	0.0008	0.051	0.0005	0.051	0.0006	0.051	
Ni	ND	19.44	0.58	16.89	0.47	20.44	0.32	19.10	0.17	20.28	0.34	20.44	
Pb	ND	0.69	0.12	0.58	0.18	0.74	0.03	0.68	0.06	0.74	0.08	0.74	
Se	ND	5	0.14	5	ND	5	0.36	5	ND	5	0.21	5	
Zn	ND	44.08	1.07	38.30	1.73	46.36	1.52	43.32	3.78	46.00	1.79	46.36	

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- A) Cr (VI) criterion is applied
- B) Hardness adjustment is inapplicable for Cr (VI), Hg and Se
- C) Human Health Criterion (fish consumption) is applied for As and Hg

ND - Not detected

<sup>\*</sup> Fresh Water Aquatic Life Chronic HAC

Table 8: Station B324 (Miller Run) Water Column Data

Sampling Date	Sampling Date 5/21/01		6/11/01		7/2	7/25/01		7/30/01		3/02	4/25/02	
Hardness (mg/l)	68	.73	76.65		81.45		45		79.65		60.9	
Analyte	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)
As	0.69	41	0.37	41	0.76	41	0.68	41	0.42	41	0.32	41
Cd	ND	1.70	0.02	1.84	0.02	1.92	0.02	1.24	0.01	1.89	0.03	1.55
Cr	1.04	11	1.03	11	1.03	11	0.71	11	0.83	11	0.83	11
Cu	3.35	6.50	1.23	7.14	1.38	7.52	2.19	4.53	1.32	7.37	2.59	5.86
Hg	0.0028	0.051	0.0007	0.051	0.0006	0.051	0.0015	0.051	0.0007	0.051	0.0013	0.051
Ni	1.88	37.87	1.34	41.53	0.88	43.72	1.06	26.47	0.25	42.90	1.32	34.19
Pb	0.37	1.67	0.05	1.88	0.10	2.01	0.10	1.04	0.04	1.96	0.23	1.46
Se	0.45	5	1.11	5	1.00	5	0.79	5	0.51	5	0.58	5
Zn	7.11	85.98	2.82	94.31	2.38	99.29	5.06	60.06	1.90	97.42	9.12	77.61

<sup>\*</sup> Fresh Water Aquatic Life Chronic HAC

- A) Cr (VI) criterion is applied
- B) Hardness adjustment is inapplicable for Cr (VI), Hg and Se
- C) Human Health Criterion (fish consumption) is applied for As and Hg

ND - Not detected

Table 9: Station B411 (East Branch of Herbert Run) Water Column Data

Sampling Date	5/21/01		6/11/01		7/25/01		7/30/01		4/3/02		4/25/02	
Hardness (mg/l)	27.45		94.8		113.4		43.8		96.15		76.8	
Analyte	Sample (µg/l)	Criteria* (µg/l)										
As	0.62	41	ND	41	0.33	41	0.43	41	0.30	41	0.52	41
Cd	0.03	0.86	0.06	2.15	0.03	2.46	0.03	1.21	0.03	2.17	0.04	1.84
Cr	1.12	11	0.28	11	ND	11	0.34	11	0.18	11	0.27	11
Cu	5.36	2.97	2.17	8.56	1.71	9.97	3.48	4.42	1.98	8.66	5.36	7.15
Hg	0.0129	0.051	0.0029	0.051	0.0027	0.051	0.0044	0.051	0.0024	0.051	0.0032	0.051
Ni	2.13	17.42	3.07	49.71	2.35	57.84	2.02	25.87	2.92	50.31	3.66	41.60
Pb	1.45	0.60	0.16	2.37	0.20	2.89	0.56	1.01	0.05	2.41	0.50	1.89
Se	0.45	5	0.77	5	1.31	5	0.56	5	0.70	5	0.86	5
Zn	15.50	39.51	8.56	112.91	7.04	131.42	8.64	58.70	7.23	114.27	15.88	94.46

Table 10: Station H171 (Deep Run) Water Column Data

Sampling Date	6/11/01		7/25/01		7/30/01		4/3	/02	4/25/02	
Hardness (mg/l)	53.55		61	.65	41.55		62.85		53.25	
Analyte	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)			Criteria* (µg/l)
As	0.14	41	0.24	41	0.69	41	0.23	41	0.31	41
Cd	0.02	1.41	0.01	1.56	0.02	1.17	0.02	1.59	0.01	1.40
Cr	0.30	11	ND	11	0.36	11	ND	11	0.07	11
Cu	1.68	5.25	1.07	5.92	2.04	4.23	1.17	6.02	1.65	5.23
Hg	0.0015	0.051	0.0008	0.051	0.0022	0.051	0.0010	0.051	0.0008	0.051
Ni	3.79	30.66	1.78	34.54	2.25	24.74	2.52	35.11	3.47	30.52
Pb	0.19	1.27	0.13	1.48	0.26	0.96	0.05	1.51	0.07	1.26
Se	0.39	5	0.41	5	0.89	5	0.23	5	0.37	5
Zn	4.94	69.59	3.72	78.42	7.35	56.13	6.57	79.71	5.68	69.26

<sup>\*</sup> Fresh Water Aquatic Life Chronic HAC

- D) Cr (VI) criterion is applied
- E) Hardness adjustment is inapplicable for Cr (VI), Hg and Se
- F) Human Health Criterion (fish consumption) is applied for As and Hg

ND - Not detected

The range of concentrations for metals sampled in the water quality survey are as follows:

As = ND to  $0.76 \mu g/l$ 

Cd = ND to 0.06 µg/l

 $Cr = ND \text{ to } 1.12 \text{ } \mu\text{g/l}$ 

Cu = ND to 5.36 µg/l

 $Hg = ND \text{ to } 0.0129 \text{ } \mu\text{g/l}$ 

Ni = ND to 3.79 µg/l

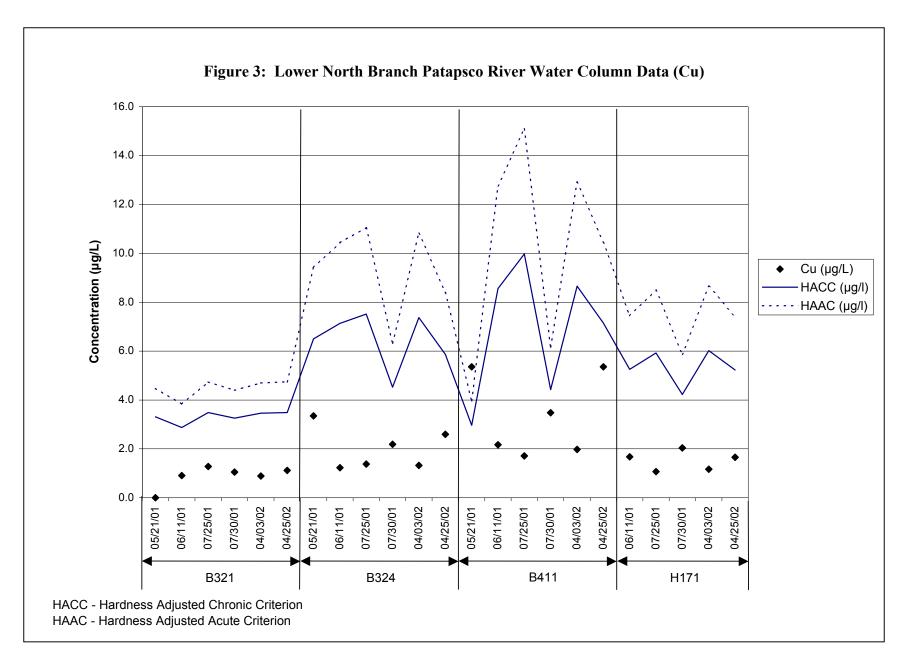
Pb = ND to 1.45 µg/l

Se = ND to 1.31  $\mu$ g/l

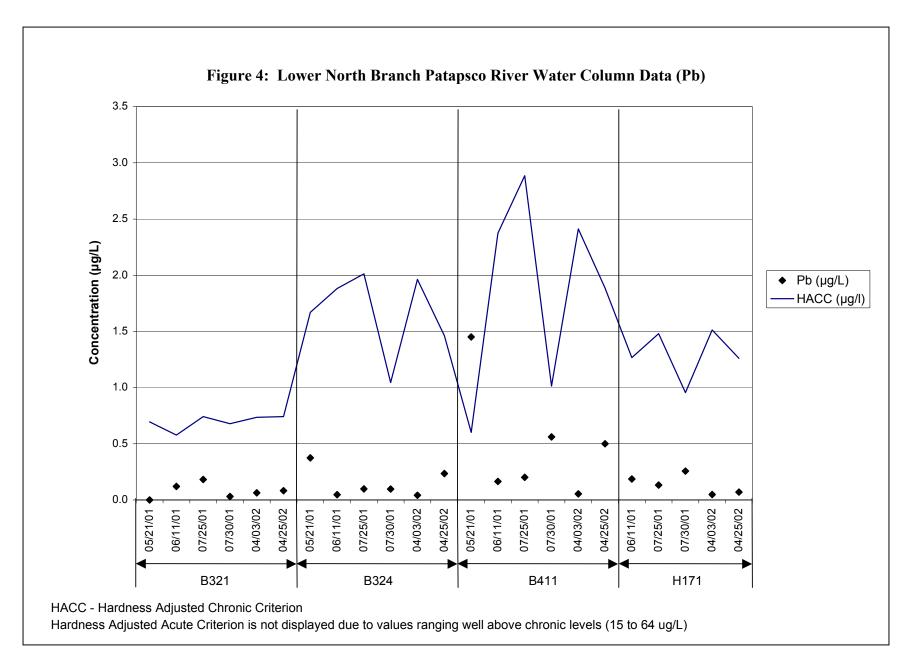
 $Zn = ND \text{ to } 15.88 \,\mu\text{g/l}$ 

Hardness ranged from 26.46 mg/l to 113.4 mg/l. A total of twenty-three samples were collected. Cu and Pb samples collected at Station B411 on May 21, 2001 exceed the hardness-adjusted chronic criteria (HACC). The remaining three stations in the watershed have no exceedances. Station B411 is located in Herbert Run, a tributary of the main branch in the lower most 12-digit basin (basin code 02-13-09-06-10-12) of the Lower North Branch Patapsco River watershed. The samples that exceeded the criteria were collected during spring storm events. Though this water quality evaluation is conducted by comparing sample concentrations versus hardness-adjusted chronic criteria (HACC), grab samples collected during storm events are only representative of an acute condition, a one-hour exposure. The chronic condition is based on an aquatic organism being exposed to a concentration over a 96-hour period. There is significant variation in the concentration profile during a storm event as contaminants are being flushed from the surface, therefore grab samples are not representative of the pollutant concentration

**FINAL** 



**FINAL** 



over a 96-hour period. In order to properly quantify a chronic concentration for a storm event it would be necessary to calculate an average of multiple samples over the 96-hour period. The Cu and Pb samples at Station B411 cannot be evaluated against the HACC thus a comparison is made using the hardness-adjusted acute criterion (HAAC) and displayed in Table 11.

**Table 11: Station B411 Water Column Exceedances** 

Sampling Date	5/21/01		
Hardness (mg/l)	27.45		
Analyte	Sample (µg/l)	HACC (µg/l)	HAAC (μg/l)
Cu	5.36	2.97	4.0
Pb	1.45	0.60	15.4

HACC – Hardness-adjusted chronic criterion HAAC – Hardness-adjusted acute criterion

Cu concentrations are higher than the HAAC and Pb concentrations are well below the HAAC. Even though the Pb concentration exceeds the HACC, the sample is not representative of the chronic condition and cannot be justifiably evaluated against the chronic criterion, therefore there is no Pb impairment.

Based on 305(b) guidance, as a first analytical step MDE applies a "rule-of-thumb" that a waterbody is impaired by a chemical contaminant in the water column when greater than 10% of the samples, with a minimum of ten samples collected over a three-year period, exceed the applicable criteria (EPA, 1997). If there are less than 10 samples for a given area, MDE may interpret the data and determine if an impairment exists by considering a number of factors including the magnitude of the criteria exceedance and number of criteria exceeded. In addition, current EPA guidelines suggest that a waterbody is not fully use-supporting when more than one exceedance of the acute or chronic water quality criterion occurs over a three-year period (EPA, 2002). With only six samples collected at station B411 and only one minimal exceedance of the HAAC, further sampling must be conducted to determine if Herbert Run is impaired for Cu. Based on this weight of evidence, the Lower North Branch Patapsco River is supportive of water quality standards except for Herbert Run. This analysis finds that a TMDL of metals is not required for the Lower North Branch Patapsco River and further investigation is required in Herbert Run to determine if a Cu impairment exists.

Sediment quality is not assessed in this WQA due to the lack of depositional areas in the Lower North Branch Patapsco River watershed. Field sampling teams observed no appreciable sediment in the streambed, as a result were unable to collect samples.

## 4.0 CONCLUSION

The WQA shows that water quality standards for metals are being achieved in the Lower North Branch Patapsco River watershed except for Herbert Run, a tributary of the main branch in the lower most 12-digit basin (basin code 02-13-09-04-10-12). Water column samples collected at five monitoring stations in the Lower North Branch Patapsco River, from May 2001 to April 2002, established that one Cu sample exceeded the applicable aquatic life criterion in Herbert Run. Therefore a TMDL for metals is not required for the Lower North Branch Patapsco River, but a TMDL for Cu may be needed in Herbert Run. Based on impairment listing methodologies applied by the Maryland Department of the Environment (MDE) further investigation is necessary to determine if Herbert Run is impaired for Cu. Additional monitoring is necessary to establish whether the exceedance was the result of a single anomalous event or further exceedances will reoccur, indicating an impairment. Barring the receipt of any contradictory data, this report will be used to support the removal of the Lower North Branch Patapsco River from Maryland's list of WQLSs for heavy metals when the Maryland Department of the Environment (MDE) proposes the revision of Maryland's 303(d) list for public review in the future. Herbert Run will remain on Part 3 (waterbodies that have insufficient data to define the impairment status) of the 303(d) list with Cu as the impairing substance.

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