Water Quality Analysis of Metals for the Little Gunpowder Falls in Harford and Baltimore Counties, Maryland

FINAL

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List of Abbreviations

As	Arsenic
CEES	Center for Estuarine and Environmental Science
CFR	Code of Federal Regulations
cfs	Cubic Feet per Second
COMAR	Code of Maryland Regulation
Cr	Chromium
Cu	Copper
CWA	Clean Water Act
DHMH	Department of Health and Mental Hygiene
DNR	Department of Natural Resources
EPA	Environmental Protection Agency
Hg	Mercury
m	Meters
MDA	Maryland Department of Agriculture
MDE	Maryland Department of the Environment
mg/l	Milligrams Per Liter
mi^2	Square miles
NCHF	North Central Hardwood Forest
NGP	Northern Glaciated Plain
Ni	Nickel
NLF	Northern Lakes and Forest
Pb	Lead
Se	Selenium
T	Temperature
USGS	United States Geologic Survey
WQLS	Water Quality Limited Segment
*u*g/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 (EPA)'s implementing regulations direct each state to identify and list waters, known as water quality limited segments (WQLSs), in which current required controls of a specified substance are inadequate to achieve water quality standards. For each WQLS, the State is to either establish a Total Maximum Daily Load (TMDL) of the specified substance that the waterbody can receive without violating water quality standards, or demonstrate that water quality standards are being met.

The Little Gunpowder Falls (basin code 02-13-08-04) was identified on the State's 1996 list of WQLSs as impaired by heavy metals and nutrients. This report provides an analysis of recent monitoring data, which shows that the aquatic life criteria and designated uses associated with heavy metals are being met in the Little Gunpowder Falls. The analysis supports the conclusion that a TMDL of heavy metals is not necessary to achieve water quality standards in this case. Barring the receipt of any contradictory data, this report will be used to support the removal of Little Gunpowder Falls from Maryland's list of WQLSs for heavy metals when MDE proposes the revision of Maryland's 303(d) list for public review in the future. The nutrient listing will be addressed separately at a future date.

Although the waters of the Little Gunpowder Falls do not display signs of toxic impairments due to heavy metals, the State reserves the right to require additional pollution controls in the Little Gunpowder Falls watershed if evidence suggests that 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 standards are being met); 2) more recent and updated water quality modeling demonstrates that the segment is now attaining standards; 3) refinements to water quality standards, or the interpretation of those standards, which result in standards being met; or 4) correction to errors made in the initial listing.

The Little Gunpowder Falls 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 and nutrients (Fischer, 1984). The initial listing for heavy metals was questionable due to the fact that: 1) no specific pollutants were defined; 2) the original listing was based on total recoverable metals (current standard is for dissolved metals); 3) outdated sampling techniques (lack of filtration) were applied; 4) water quality criteria dependent data such as hardness was not obtained; and, 5) 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 of heavy metals was performed more recently using current sampling and analytical techniques, which shows no impairment for the Little Gunpowder Falls.

The terms "metals" and "heavy metals" are used interchangeably and are generally interpreted to include those metallic elements from periodic table groups IIA through VIA. Throughout the body of the report the word "metals" will be used to indicate heavy metals. 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 water quality analysis, metals are those priority pollutant metals that are commonly permitted in NPDES industrial or NPDES stormwater discharges. The following metals were monitored in the Little Gunpowder Falls basin: arsenic (As), cadmium (Cd), chromium III (Cr-III), 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 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, monitoring 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 Little Gunpowder Falls watershed, presents a discussion of the water quality characterization process, and provides conclusions with regard to the characterization. The most recent data establishes that the Little Gunpowder Falls is achieving water quality standards for metals.

2.0 GENERAL SETTING

The Little Gunpowder Falls watershed is located in the Upper Western Shore region of the Chesapeake Bay watershed within Maryland (see Figure 1). The watershed covers portions of Baltimore and Harford counties. The watershed area covers 37,340 acres.

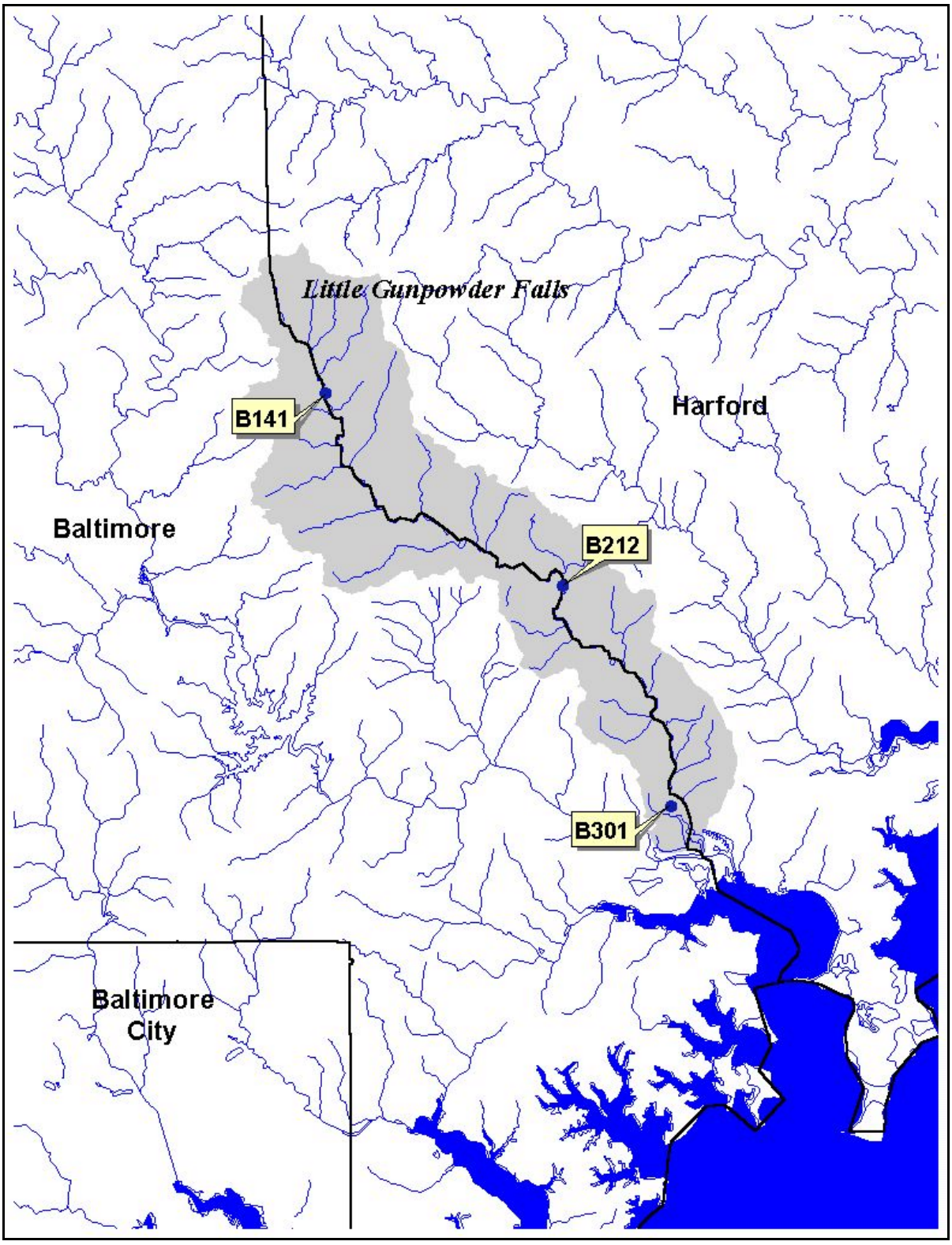

Figure 1: Watershed Map of the Little Gunpowder Falls, Maryland

The Little Gunpowder Falls 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, 1995).

The Little Gunpowder Falls watershed drains from northwest to southeast, following the dip of the underlying crystalline bedrock in the Piedmont Province. The surface elevations range from approximately 680 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 and into the soft, flat Coastal Plain sediments (Coastal, 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):

> A: Soils with high infiltration rates, typically deep well-drained to excessively drained sands or gravels.
> B: Soils with moderate infiltration rates, generally moderately deep to deep, moderately well to well drained soils with moderately fine to moderately coarse textures.
> C: Soils with slow infiltration rates, mainly soils with a layer that impedes downward water movement or soils with moderately fine to fine texture.
> 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 68.9% of the B soil group, 17.2% of the C soil group, 8.1% of the D soil group, and 5.8% of the A soil group.

The Little Gunpowder Falls flows through mostly agricultural and forested lands joining the Gunpowder Falls within the Gunpowder Falls State Park before reaching the estuarine portion of the Gunpowder River. No point sources drain to the stream, or are there other apparent anthropogenic sources of pollutants. There is very little urbanization within the Little Gunpowder Falls watershed, which is comprised primarily of agricultural, forest and residential land uses (see Figure 2). The land use distribution in the watershed is approximately 43.8% agricultural, 32.1% forestland, 21.9% residential, 1.2% commercial/industrial, and 1.0 % designated as barren, open urban lands and open water.

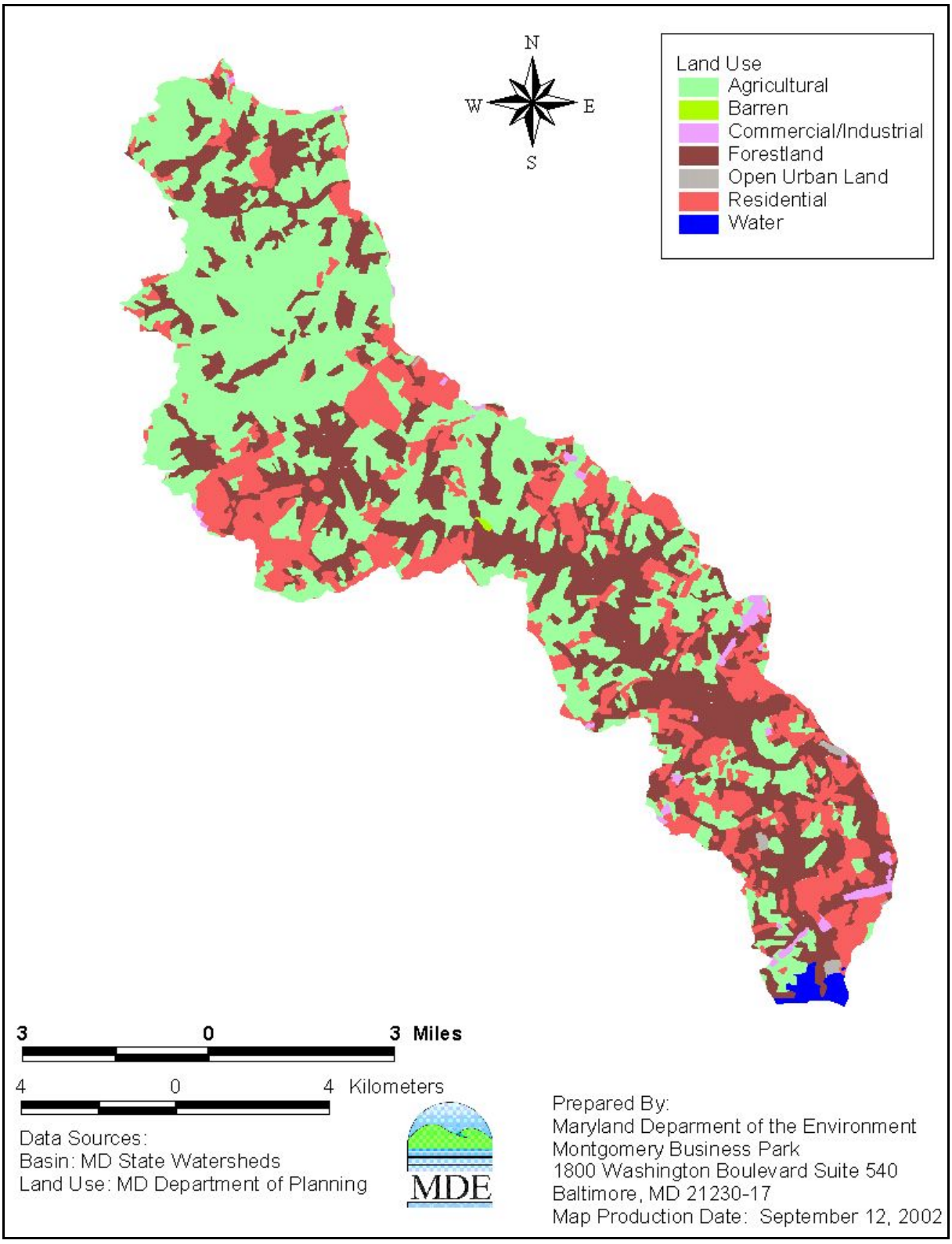

Figure 2: Land Use Map of Little Gunpowder Falls Watershed

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 activities such as aquatic life use and support, 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 impose numeric criteria for metals and other toxic substances based on the need to protect aquatic life, wildlife and human health

The Maryland Surface Water Use Designation (COMAR 26.08.02.07) for the Gunpowder River (Basin code 02-13-08) and its tributaries (including Little Gunpowder Falls) is Use III – *natural trout waters*. The applicable numeric criteria for metals (dissolved phase) in freshwater is described below in Table 1 (COMAR 26.08.02.03-3G). The water quality data present in this section will show that the water quality standards are being met; therefore, the designated use of the Little Gunpowder Falls is not impaired by metals contamination.

Table 1: Freshwater Aquatic Life Criteria For Inorganic Substances (Metals)

Metal	Aquatic Life Acute (CMC) (ug/L)	Aquatic Life Chronic (CCC) (ug/L)
As	340	150
Cd	4.3	2.2
Cr (III)	570	74
Cu	13	9
Hg	1.4	0.77
Ni	470	52
Pb	65	2.5
Se	20	5
Zn	120	120

Water quality surveys conducted at three stations in the Little Gunpowder Falls watershed from May 2001 to April 2002 were used for this analysis. The nine metals presented in Table 1 were sampled for dissolved concentrations. Table 2 shows the list of stations with their geographical coordinates and descriptive location in the Little Gunpowder Falls. The station locations are presented in Figure 1.

Table 2: Water Quality Analysis Stations for Little Gunpowder Falls, Maryland.

#	Station I.D.	GPS coordinates	Station Description
1	B141	39°34.34' 76°46.35'	1/2 mile South East of Mt Zion Church
2	B212	39°30.27' 76°25.80'	Little Gunpowder Falls @ Laurel Brook, MD
3	B301	39°25.46' 76°22.66'	Old Philadelphia Road

3.1 Metals Data

Sampling was performed six times at each station from May 2001 to April 2002 to capture seasonal variation. Three sampling periods were taken during wet weather and the other three, during dry weather. The dates of the sampling periods were as follows: 5/21/01 (Spring wet weather), 6/11/01 (Spring dry weather), 7/25/01 (Summer dry weather), 7/30/01 (Summer wet weather), 4/3/02 (Spring wet weather) and 4/25/02 (Spring dry weather).

Hardness concentrations were obtained for each station to adjust the EPA standard water quality criteria, established at a hardness of 100 mg/L. The hardness adjusted criteria (HAC) equation for heavy metals is as follows:

$$HAC = e^{(m[\ln (Hardness)]+b)} * CF \qquad \text{(EPA, 1996)}$$

HAC = Hardness Adjusted Criteria
m = slope
b = y intercept
CF = Conversion Factor

The hardness adjusted criteria parameters for metals are presented in Table 3.

Table 3: Hardness Adjusted Criteria Parameters

Chemical	Slope (m)	y Intercept (b)	Conversion Factor (CF)
Cd	0.7852	-2.715	0.909
Cu	0.8545	-1.702	0.960
Cr (III)	0.8190	0.685	0.860
Pb	1.2730	-4.705	0.791
Ni	0.8460	0.0584	0.997
Zn	0.8473	0.884	0.986

A direct comparison of the EPA standard water quality criteria and As, Se and Hg concentrations was performed 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 the Revised Aquatic Life Metals Criteria in EPA's National Toxics Rule (EPA, 1995), allowable hardness values must fall within the range of 25 - 400 mg/L. Based on technical information, EPA's Office of Research and Development does not recommend a lower limit on hardness for adjusting criteria.

The water quality data (Baker, 2001) is presented in Tables 3A – 3F for each sampling period. Each table displays the EPA standard water quality criteria along with the sample concentration and hardness adjusted criteria concentration for Zn at each station. Sample concentrations are listed in columns headed by the station I.D. Hardness adjusted criteria are listed in columns headed by "HAC" followed by the station I.D. The first row of the table reports the hardness concentrations for each station. Criteria and dissolved metals concentrations are expressed as ug/L and hardness is expressed as mg/L. As an example in Table 3B, for station B141 the hardness is 16.62 mg/L, the standard water quality criteria for Cu is 9, the hardness adjusted criteria for Cu is 4.95 ug/L and the Cu concentration is 0.51 ug/L.

Table 3A. 5/21/01 Spring Wet Weather

Analyte	Criteria *	HAC ** B141	B141	HAC ** B212	B212	HAC ** B301	B301
Hardness		HND		HND		HND	
As	150	-	ND	-	ND	-	0.19
Cd	2.2	-	ND	-	ND	-	ND
Cr (III)	74	-	0.29	-	0.2	-	0.21
Cu	9	-	0.73	-	0.63	-	0.88
Hg***	0.051	-	0.00102	-	0.00047	-	0.00092
Ni	52	-	0.53	-	0.31	-	0.32
Pb	2.5	-	0.07	-	0.04	-	0.06
Se	5	-	ND	-	ND	-	0.19
Zn	120	-	0.81	-	0.57	-	0.78

* EPA Fresh Water Chronic Criteria are expressed in µg/L (ppb)
** Criteria adjusted for ambient hardness
***EPA's criteria for preventing fish tissue accumulation of mercury
HAC = Hardness Adjusted Criteria
HND - Hardness not determined
ND - Not detected

Table 3B: 6/11/01 Spring Dry Weather

Analyte	Criteria *	HAC ** B141	B141	HAC ** B212	B212	HAC ** B301	B301
Hardness		16.62		18.735		19.65	
As	150		ND		ND		ND
Cd	2.2	1.3	ND	0.6	ND	0.7	ND
Cr (III)	74	17	0.18	18.8	0.24	19.6	0.23
Cu	9	4.95	0.51	2.14	0.45	2.23	0.57
Hg***	0.051	-	0.00061	-	0.00044	-	0.00064
Ni	52	28.9	0.31	12.6	0.28	13.1	0.27
Pb	2.5	1.2	0.07	0.4	0.05	0.4	0.04
Se	5	-	0.15	-	0.2	-	0.22
Zn	120	65.7	0.58	28.6	0.36	29.8	0.31

* EPA Fresh Water Chronic Criteria are expressed in µg/L (ppb)
** Criteria adjusted for ambient hardness
***EPA's criteria for preventing fish tissue accumulation of mercury
HAC = Hardness Adjusted Criteria
HND - Hardness not determined
ND - Not detected

Table 3C: 7/25-26/01 Summer Dry Weather

Analyte	Criteria *	HAC ** B141	B141	HAC ** B212	B212	HAC ** B301	B301
Hardness		18.945		21.12		23.445	
As	150	-	0.24	-	0.18	-	0.2
Cd	2.2	0.7	ND	0.7	ND	0.8	ND
Cr (III)	74	19	0.25	20.7	0.05	22.6	0.17
Cu	9	2.16	0.49	2.37	0.49	2.59	0.63
Hg***	0.051	-	0.00067	-	0.00071	-	0.00061
Ni	52	12.7	0.26	14	0.13	15.2	0.21
Pb	2.5	0.4	0.07	0.4	0.04	0.5	0.04
Se	5	-	ND	-	ND	-	ND
Zn	120	28.9	0.49	31.6	0.31	34.6	0.48

Table 3D: 07/30/01 Summer Wet Weather

Analyte	Criteria *	HAC ** B141	B141	HAC ** B212	B212	HAC ** B301	B301
Hardness		19.815		21.54		23.325	
As	150	-	0.06	-	0.09	-	0.22
Cd	2.2	0.7	ND	0.7	ND	0.8	ND
Cr (III)	74	19.7	0.1	21.1	0.07	22.5	0.05
Cu	9	2.25	0.37	2.41	0.42	2.58	0.62
Hg***	0.051	-	0.0008	-	0.0005	-	0.00051
Ni	52	13.2	0.21	14.2	0.17	15.2	0.15
Pb	2.5	0.4	ND	0.5	ND	0.5	ND
Se	5	-	0.14	-	ND	-	0.3
Zn	120	30	0.37	32.2	0.37	34.4	0.86

* EPA Fresh Water Chronic Criteria are expressed in µg/L (ppb)
** Criteria adjusted for ambient hardness
***EPA's criteria for preventing fish tissue accumulation of mercury
HAC = Hardness Adjusted Criteria
HND - Hardness not determined
ND - Not detected

Table 3E: 04/3/02 Spring Dry Weather

Analyte	Criteria *	HAC ** B141	B141	HAC ** B212	B212	HAC ** B301	B301
Hardness		18.15		18.45		23.49	
As	150	-	0.13	-	0.14	-	0.14
Cd	2.2	0.6	ND	0.6	ND	0.8	ND
Cr (III)	74	18.3	0.07	18.6	0.08	22.6	0.08
Cu	9	2.08	0.37	2.11	0.40	2.6	0.63
Hg***	0.051	-	0.00074	-	0.00066	-	0.00063
Ni	52	12.3	0.18	12.4	0.08	15.3	0.12
Pb	2.5	0.4	0.03	0.4	0.03	0.5	0.03
Se	5	-	ND	-	ND	-	ND
Zn	120	27.8	0.28	28.2	0.25	34.6	0.50

Table 3F: 04/25/02 Spring Wet Weather

Analyte	Criteria *	HAC ** B141	B141	HAC ** B212	B212	HAC ** B301	B301
Hardness		17.79		19.92		22.89	
As	150	-	ND	-	ND	-	0.19
Cd	2.2	0.6	ND	0.7	ND	0.8	ND
Cr (III)	74	18	0.04	19.8	ND	22.2	0.06
Cu	9	2.05	0.38	2.26	0.45	2.54	0.72
Hg***	0.051	-	0.00063	-	0.00071	-	0.00102
Ni	52	12.1	0.20	13.3	0.16	14.9	0.19
Pb	2.5	0.4	0.03	0.4	0.03	0.5	0.04
Se	5	-	0.19	-	0.20	-	0.17
Zn	120	27.4	0.41	30.1	0.27	33.9	0.87

* EPA Fresh Water Chronic Criteria are expressed in µg/L (ppb)
** Criteria adjusted for ambient hardness
***EPA's criteria for preventing fish tissue accumulation of mercury
HAC = Hardness Adjusted Criteria
HND - Hardness not determined
ND - Not detected

The range of concentrations for metals sampled in the water quality survey are as follows: As (0.06 to 0.24), Cr (0.04 to 0.29), Cu (0.37 to 0.88), Hg (0.00044 to 0.00102), Ni (0.08 to 0.53), Pb (0.03 to 0.07), Se (0.14 to 0.3) and Zn (0.25 to 0.87). All concentrations are reported in ug/L. Hardness ranged from 16.6 to 23.4 (mg/L). The concentration ranges of all nine metals are well below the fresh water chronic hardness-adjusted criteria. The criteria was not exceeded by any of the nine metals sampled.

4.0 CONCLUSION

The water quality analysis shows no violation of water quality criteria for any metals evaluated. The data demonstrates that water quality in the Little Gunpowder Falls basin meet water quality standards for metals, and can be removed from the impaired waters list for "heavy metals". Based on the synoptic survey conducted from May 2001 to April 2002, the water quality data indicate that the Little Gunpowder Falls does not have toxics-related water quality problems pertaining to metals contamination. Barring any contradictory future data, this information provides sufficient justification to revise Maryland's 303(d) list to remove metals as an impairing substance in relation to the 8-digit Little Gunpowder Falls.

5.0 REFERENCES

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