Water Quality Analysis of Arsenic, Cadmium and Silver in Back Creek, Cecil County, Maryland

FINAL

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List of Abbreviations

Ag	Silver
As	Arsenic
AVS	Acid Volatile Sulfide
CBL	Chesapeake Biological Laboratory
Cd	Cadmium
cm	Centimeter
COMAR	Code of Maryland Regulations
Cr	Chromium
Cu	Copper
CWA	Clean Water Act
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency
ERL	Effects Range Low
ERM	Effects Range Median
FWCC	Freshwater Chronic Criteria
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
mg/l	Milligrams per Liter
NPDES	National Pollution Discharge Elimination System
NWS	National Weather Service
Pb	Lead
PCBs	Polychlorinated biphenyls
ppt	Parts per Thousand
SCS	Soil Conservation Service
SEM	Simultaneously Extracted Metals
SHA	State Highway Administration
STATSGO	State Soil Geographic
SQG	Sediment Quality Guideline
TEC	Threshold Effects Concentration
TEL	Threshold Effects Limit
TMDL	Total Maximum Daily Load
UMCES	University of Maryland Center for Environmental Science
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 currently required controls of a specified substance are inadequate to achieve water quality standards. For each WQLS, the State is required 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.

Back Creek (basin code 02-13-06-04), located in Cecil County, MD, was identified on the State's list of WQLSs as impaired by nutrients (1996 listing), suspended sediments (1996 listing), arsenic (As) (1996 listing), cadmium (Cd) (1996 listing) and silver (Ag) (1996 listing). All impairments were listed for tidal waters. Code of Maryland Regulations [(COMAR) 26.08.02.03-1(B)(3)(g)] defines the Elk River, which includes the Back Creek tributary, as a fresh waterbody. The information used for listing Ag, As, and Cd was obtained from an 1989 study that is suspect due in part to sampling and analysis methods available at the time, and assessment inconsistencies that led to the listing in 1996 (P.Jiapizian, personal communication, 2001).

This report provides an analysis of recent monitoring data, including hardness data, which shows that the aquatic life uses and criteria are not impaired by As, Cd, and Ag in the Back Creek watershed, and the 303(d) impairment listings associated with As, Cd and Ag are not supported by the analyses contained herein. The analyses support the conclusion that TMDLs for As, Cd and Ag are 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 the Back Creek from Maryland's list of WQLSs for As, Cd and Ag 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 nutrients and suspended sediments will be addressed separately at a future date.

Although the information supporting this water quality analysis demonstrates that toxic impairments due to As, Cd or Ag are not likely, there is also a realization that sediment toxicity exists as evidenced by the results of the 28 day amphipod (L. plumulosus) sediment toxicity tests. The state will therefore remove As, Cd, and Ag as impairing substances, but will relist the segment (2006 303(d) list, Part V) for aquatic life use impairments due to sediment toxicity (unidentified contaminants). The new listing will be available for public review in the late fall 2005. This will require the State to perform additional studies in this area to identify the contaminant(s) responsible for causing the observed sediment toxicity. Finally, although the waters of the Back Creek watershed do not display signs of toxic impairments due to As, Cd or Ag, the State reserves the right to require additional pollution controls in the Back Creek watershed if evidence suggests that As, Cd or Ag 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 currently 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 required 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 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.

Back Creek (basin code 02-13-06-04) was identified on the State's 1996 303(d) list as impaired by nutrients, suspended sediments, arsenic (As), cadmium (Cd) and silver (Ag). All impairments were listed for tidal waters. Code of Maryland Regulations (COMAR 26.08.02.03-1(B)(3)(g)) defines the Elk River, which includes the Back Creek tributary, as a fresh waterbody.

The informational basis, a study completed in 1989, for this listing showed that mean levels of As, Cd, and Ag exceeded the EPA Maximum Contaminant Limit (MCL), a drinking water threshold established through the Safe Drinking Water Act (SDWA), and not the CWA (P. Jiapizian, personal communication, 2001). Use of SDWA thresholds for designated use assessments pursuant to CWA 303(d) are inappropriate in this case since this segment is not designated as a public water supply. Also, both the acute and chronic aquatic life criteria were exceeded for both Cd and Ag at the time of listing.

Although criteria were "exceeded," several methodological flaws exist in the monitoring and listing assessment used in 1996. First, unfiltered (total metals) samples were compared to dissolved criteria. Second, current criteria for Ag and 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. This water quality analysis demonstrates that hardness varied from 58 to greater than 400 mg/L, with three out of four samples above 100 mg/L. This is important since elevated hardness mitigates potential toxicity by reducing bioavailability of the metals at the gill epithelia in sensitive aquatic receptors. 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 Ag, As, and Cd have appropriate detection limits that are well below their respective criteria values (except in the case of waters with very low hardness values).

A Water Quality Analysis (WQA) of As, Cd and Ag for the tidal waters of Back Creek 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. Results show no impairment for As, Cd and Ag. This report will be used to support the removal of the 8-digit basin from Maryland's list of WQLSs for As, Cd and Ag. Accordingly, TMDLs for As, Cd and Ag are not required for Back Creek. The nutrient and sediment impairments will be addressed separately at a future date.

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

2.0 GENERAL SETTING

The Back Creek watershed is located in the Upper Eastern Shore region of the Chesapeake Bay watershed within Maryland (see Figure 1). The watershed covers a portion of Cecil County. The watershed area is 8,729 acres.

The Chesapeake & Delaware Canal is located in the Back Creek watershed. The canal was constructed in 1829 to create a shipping lane between the Chesapeake Bay and Delaware River. Over 40% of all shipping traffic in and out of the Port of Baltimore travels through the canal. The canal is currently operated by the U.S. Army Corp of Engineers and is the only major commercial shipping canal operating in the U.S. today. The only major community in Back Creek, Chesapeake City, is located on both sides of the entrance to the canal. The city was founded in response to the growing needs of canal operations and commerce.

The Back Creek watershed lies within the Atlantic Coastal Plain province of Eastern Maryland. 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 watershed is comprised 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 alay soils, soils with a

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.

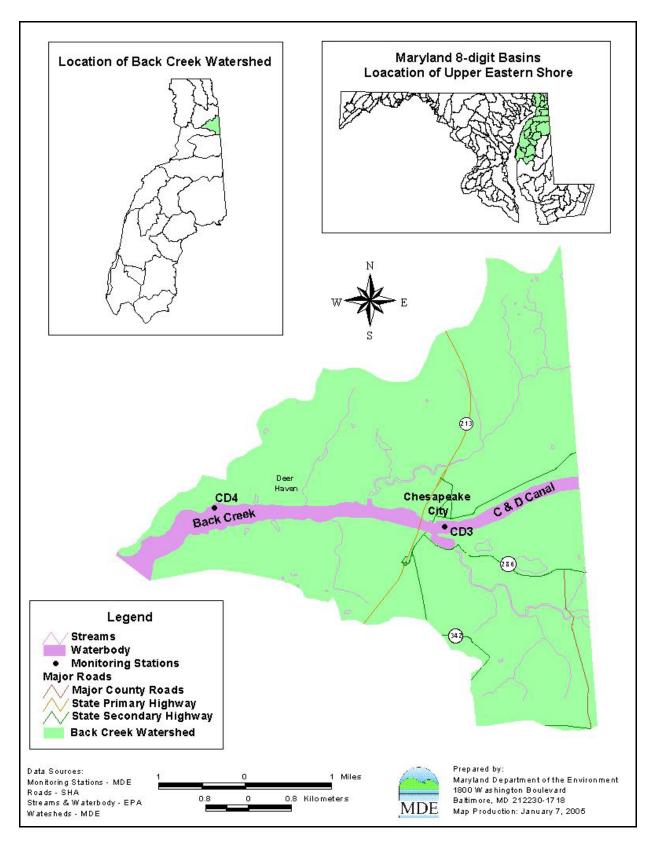


Figure 1: Watershed Map of the Back Creek

The soil distribution within the watershed is approximately 55 % soil group B and 45 % soil group C. Soil data was obtained from State Soil Geographic (STATSGO) coverages created by the National Resources Conservation Service.

The Back Creek watershed is comprised primarily of agricultural and forested land uses (see Figure 2). There are no major industrial or municipal facilities discharging As, Cd or Ag within the watershed. The land use distribution in the watershed is approximately 38.2 % forest/herbaceous, 46.8 % agricultural, 10.7 % urban and 4.3 % water (Maryland Department of Planning, 2002).

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 26.08.02.08-G(2)(a)) for the Elk River (basin code 02-13-06) and its tributaries (including Back Creek) is Use I - water contact recreation, fishing, and protection of aquatic life and wildlife. COMAR 26.08.02.03-1(B)(3)(g) defines the tidal region of the Back Creek watershed considered in this WQA as being freshwater even though salinity concentrations are found to exceed one ppt. Based on EPA guidance, when salinity concentrations are between one and ten ppt the more stringent of the freshwater and saltwater aquatic life criteria are applied (EPA, Nov 2002). The freshwater and saltwater aquatic life criteria (default hardness = 100 mg/L) for As, Cd and Ag are displayed below in Table 1 (COMAR 26.08.02.03-2(G)). The water column data presented in Section 3.1, Table 4 and Table 5, show that concentrations of As, Cd and Ag in the water column do not exceed water quality criteria. An ambient sediment bioassay conducted by the University of Maryland Wye Research Center and sediment chemistry analysis conducted by the University of Maryland Center for Environtmental Science (UMCES) in the Back Creek establishes that there is no toxicity in the sediment bed as a result of As, Cd or Ag contamination. The water column and sediment in the Back Creek are, therefore, not impaired by As, Cd or Ag. Thus the designated uses are supported and the water quality standards are being met.

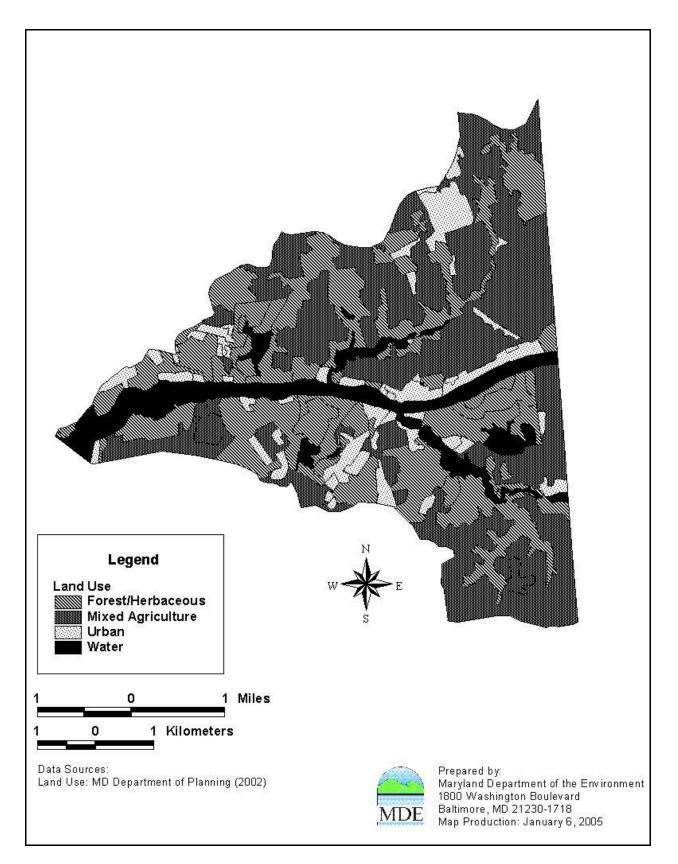


Figure 2: Land Use Map of Back Creek Watershed

Metal	Fresh Water Aquatic Life Acute Criteria (µg/l)	Fresh Water Aquatic Life Chronic Criteria (µg/l)	Salt Water Aquatic Life Acute Criteria (µg/l)	Salt Water Aquatic Life Chronic Criteria (µg/l)
As	340	150	69	36
Ag	3.2	-	1.9	-
Cd	2	0.25	40	8.8

* Criteria based on default hardness of 100 mg/L (Saltwater criteria and As are not subject to hardness adjustment)

Water column surveys, used to support this WQA, were conducted by UMCES at two stations throughout the Back Creek estuary from March 2003 to October 2003. For every water column sample, the dissolved concentration of As, Cd and Ag and hardness were measured. Water column sampling was performed four times at each station to capture seasonal variation. The sampling dates were as follows: 3/12/03 (winter dry weather); 4/16/03 (spring wet weather); 6/25/03 (spring dry weather); 10/01/03 (fall wet weather). Sediment bulk samples were also collected once on 10/01/03 at each station. Sediment samples were chemically analyzed for total metals in the sediment, dissolved metals in the porewater and toxicity using a standard EPA 28 day amphipod test. Table 2 shows the list of stations with their geographical coordinates and descriptive locations. The station locations are displayed in Figure 1.

 Table 2: Sample Stations for Back Creek

Station	Latitude	Longitude	Description
CD3	39.529 -75.809 Across channel from Watty Po		Across channel from Watty Point
CD4	39.532	-75.858	Center of channel near Chesapeake City

For the water quality evaluation, a comparison is made between As, Cd and Ag dissolved water column concentrations and the fresh water aquatic life chronic criteria, the most stringent of the numeric water quality criteria for As, Cd and Ag. When salinity concentrations exceed 1 ppt, but are below 10 ppt, the more stringent of the freshwater and saltwater criteria are applied. Freshwater and saltwater chronic criteria do not exist for Ag, therefore the acute criteria are applied. Water hardness concentrations were obtained for each station to adjust the fresh water criteria that were established at a default hardness of 100 mg/l for Cd and Ag (COMAR 26.08.02.03-2(G)).

The State uses a water hardness adjustment to calculate fresh water criteria for those metals (Cd and Ag) for which toxicity is a function of total hardness (EPA, November 2002). With no available freshwater chronic criterion for Ag, the freshwater acute criterion is adjusted for

hardness. The fresh water criteria is not adjusted for As because hardness either does not affect the bioavailability of this metal 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, 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 criteria (EPA, July 2002). A lower limit may result in criteria that is less protective of the water quality standard.

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

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

Where,

HAC = Hardness Adjusted Criteria (ug/l) m = Slopeb = v Intercept CF = Conversion Factor (conversion from totals to dissolved numeric criteria)

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

Chemical	emical Criteria Slope (m)		y Intercept (b)	Conversion Factor (CF)	
Cd	Chronic	0.7409	-4.719	1.102 - In(hardness)*0.0418	
Ag	Acute	1.72	-6.59	0.85	

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

3.1 WATER COLUMN EVALUATION

A data solicitation for As, Cd and Ag 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 and Table 5 for each station and is evaluated using the fresh water hardness adjusted chronic criteria (Baker, 2004). If salinity is greater than 1ppt the more stringent of the freshwater and saltwater criteria is applied. Each table displays hardness (mg/l), sample concentration $(\mu g/l)$, detection limit $(\mu g/l)$ and criteria $(\mu g/l)$ by sampling date. For example, in Table 4 for the sampling date of 10/01/03 at station CD3 the hardness is 491 mg/l (400mg/l is used for adjusting the freshwater chronic criteria because of the hardness limit), the hardness adjusted chronic criteria for Cd is 0.64 µg/l and the Cd sample concentration is 0.02 µg/l. Saltwater criteria, when applied, are displayed in bold. A hardness limit of 400 mg/l is applied for adjusting freshwater chronic criteria as defined by EPA's National Recommended Water Ouality Criteria (EPA.

2002). The water column data for As, Cd and Ag is also displayed in Figures 3, 4 and 5, respectively.

Sampli	ng Date	3/12	2/03	4/1	6/03	6/2	5/03	10/ [,]	1/03
Salint	y (ppt)	0.4	49	0.	99	0.	17	1.	60
Hardne	ss (mg/l)	14	14	28	30	5	58	491	(400)
Analyte	Detection Limit	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)
Ag	0.1	ND	6.0	ND	18.9	ND	1.3	ND	1.9
As	0.05	0.21	150	0.24	150	0.69	150	0.57	36 ^c
Cd	0.005	0.02	0.32	0.02	0.50	0.01	0.17	0.02	0.64

Table 4: Station CD3 Water Column Data

* Freshwater Aquatic Life Chronic Criteria

A) Freshwater criteria are adjusted for hardness when applicable (As criterion is not adjusted for hardness)

B) Freshwater chronic criterion for Ag does not exist therefore the acute criterion is applied and hardness adjusted

C) If salinity is greater than 1 ppt, but less than 10 ppt, the more stringent of the saltwater and freshwater criteria is applied

D) Saltwater criteria are presented in bold

ND - Not detected

If hardness is greater than 400 mg/l, a value of 400 mg/l is used in the hardness adjustment calculation.

Sampli	ing Date	3/12	2/03	4/1	6/03	6/2	5/03	10/ [,]	1/03
Salint	ty (ppt)	0.	50	0.	85	0.	17	1.	50
Hardne	ss (mg/l)	14	47	24	43	5	58	462	(400)
Analyte	Detection Limit	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)	Sample (µg/l)	Criteria* (µg/l)
Ag	0.1	ND	6.2	ND	14.8	ND	1.3	ND	1.9
As	0.05	0.20	150	0.22	150	0.51	150	0.55	36 ^c
Cd	0.005	0.02	0.32	0.02	0.46	0.01	0.17	0.02	0.64

Table 5: Station CD4 Water Column Data

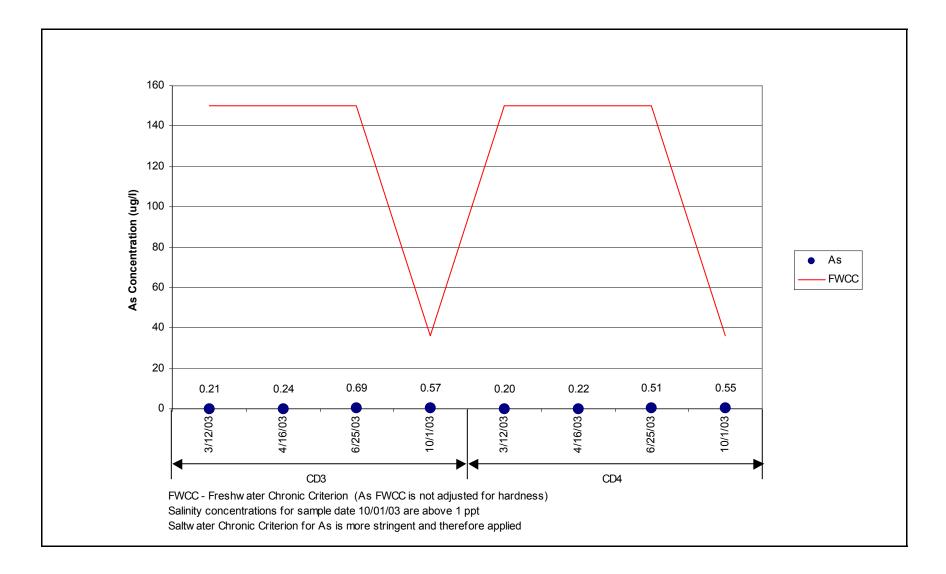


Figure 3: Back Creek Water Column Data (As)

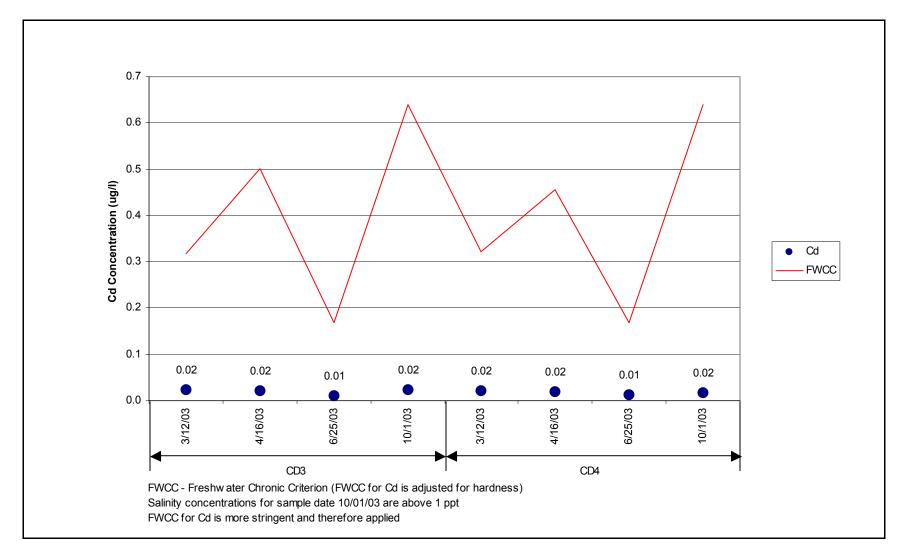


Figure 4: Back Creek Water Column Data (Cd)

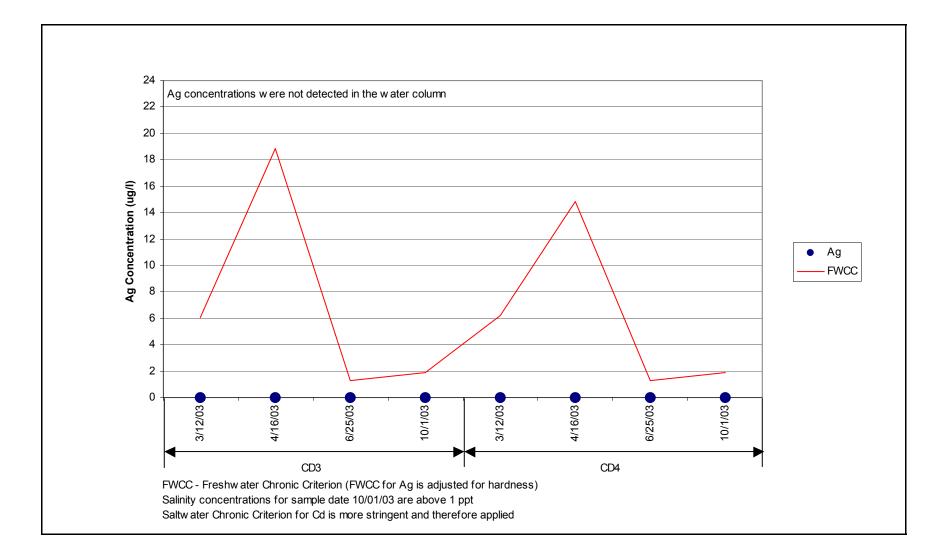


Figure 5: Back Creek Water Column Data (Ag)

The range of concentrations for As, Cd and Ag sampled in the field survey is as follows:

As - 0.20 to 0.69 Cd - 0.01 to 0.02 Ag - ND

Hardness ranged from 58 mg/l to 491 mg/l. The concentration range of As and Cd is well below the associated fresh water aquatic life HAC. Ag was not detected in the water column. All observed water column concentrations were between 1 and 2 orders of magnitude (10-100 times) lower than their respective criteria value..

An analysis of porewater concentrations was also conducted in order to evaluate the concentrations of the freely bioavailable portion of As, Cd and Ag in the sediment matrix. The pore water data is presented in Table 6 and Table 7 for each station and is evaluated using the fresh water hardness adjusted chronic criteria (Baker, 2004). This comparison is similar to what was done for the water column. If salinity is greater than 1ppt the more stringent of the freshwater and saltwater criteria is applied. Each table displays the hardness (mg/l), sample concentration (μ g/l), detection limit (μ g/l) and criteria (μ g/l) by sampling date for each station. Saltwater criteria, when applied, are displayed in bold. A hardness limit of 400 mg/l is applied for adjusting freshwater chronic criteria as defined by EPA's National Recommended Water Quality Criteria (EPA, 2002).

Sampli	ng Date	10/ <i>*</i>	1/03	
Salinit	y (ppt)	1.	60	
Hardnes	ss (mg/l)	491		
Analyte	Detection Limit	Sample (µg/l)	Criteria* (µg/l)	
Ag	0.1	ND 1.9 ^c		
As	0.05	12.5 36 ^c		
Cd	0.005	0.02 0.64		

Table 6: Station CD3 Porewater Data

* Freshwater Aquatic Life Chronic Criteria

A) Freshwater criteria are adjusted for hardness when applicable (As criterion is not adjusted for hardness)

B) Freshwater criterion for Ag does not exist therefore the acute criterion is applied and hardness adjusted

C) If salinity is greater than 1 ppt, but less than 10 ppt, the more stringent of the saltwater and freshwater criteria is applied

D) Saltwater criteria are presented in bold

ND - Not detected

If hardness is greater than 400 mg/l, a value of 400 mg/l is used in the hardness adjustment calculation.

Sampli	ng Date	10/ [,]	1/03	
Salinit	y (ppt)	1.50		
Hardnes	ss (mg/l)	46	62	
Analyte	Detection Limit	Sample (µg/l)	Criteria* (µg/l)	
Ag	0.1	ND 1.9 ^c		
As	0.05	6.5	36 ^c	
Cd	0.005	0.01	0.64	

Table 7: Station CD4 Porewater Data

The concentrations of As and Cd were between 5-10 times lower than their associated hardness adjusted chronic criteria, and Ag was not detected in the porewater. Detection limits were appropriate for the analysis. The bulk sediment and porewater analyses corroborate the assumption that toxicity to aquatic life from Ag, As, or Cd is unlikely through either a porewater exposure and/or sediment ingestion scenario based on the information provided.

3.2 SEDIMENT QUALITY EVALUATION

To complete the WQA, sediment quality in the Back Creek was evaluated using a standard 28day whole sediment test with the estuarine amphipod *Leptocheirus plumulosus* (Fisher, 2004). This species was chosen because of its ecological relevance to the waterbody of concern. *L. plumulosus* is an EPA-recommended test species for assessing the toxicity of marine and estuarine sediments (EPA, March 2001). Two surficial sediment samples were collected using a petite ponar dredge (top 2 cm) in the Back Creek. 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. The results are presented in Table 8. Five replicates containing twenty amphipods each were exposed to the contaminated sediment, as well as a control sediment, for testing. The table displays amphipod survival (#), amphipod growth rate (mg/day), amphipod reproduction (# of neonates), average amphipod survival (%), average amphipod growth rate (mg/day) and average amphipod reproduction (neonates per survivor).

Sample	Amphipod Survival (#)	Amphipod Growth Rate (mg/day)	Reproduction (# of Neonates)	Average Amphipod Survival (%)	Average Amphipod Growth Rate (mg/day)	Average Amphipod Reproduction (Neonates/survivor)	
Control A	15	0.018	12				
Control B	15	0.013	15		0.022		
Control C	17	0.019	13	80.0		1.17	
Control D	16	0.025	25				
Control E	17	0.034	27				
C&D 3 A	7	0.014	4				
C&D 3 B	6	0.012	1		0.017		
C&D 3 C	15	0.023	18	57.0		0.47	
C&D 3 D	16	0.021	4				
C&D 3 E	13	0.017	2				
C&D 4 A	5	0.013	0				
C&D 4 B	4	0.011	0				
C&D 4 C	11	0.009	0	26.0 *	0.008	0.00	
C&D 4 D	6	0.008	0				
C&D 4 E	0	0	0				

Table 8: Sediment Toxicity Test Results

* Sample Toxicity (field value significantly less than control value)

Treatments significantly different for survival not tested for sublethal endpoint significance

The test considers three performance criteria, which are survival, growth rate, and reproduction. For the test to be valid the average 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. The average survival for control samples is 80%. The average survival for stations CD3 and CD4 was 57% and 26%, respectively. The average survival for CD4 was significantly less than the average survival demonstrated in the control samples while the average survival for CD3 was not significantly less than the control. This comparison was made using Fisher's Least Significance Difference (LSD) test ($\alpha = 0.05$). Station CD4 exhibited toxicity contributing to mortality. Field samples that are significantly different for survival are not tested for significant difference between the control and field samples for amphipod growth and reproduction.

The measurable average amphipod reproduction observed in the field sediment samples was 0.47 and 0 for stations CD3 and CD4, respectively. The reproduction for station CD3 was not significantly less than the reproduction of 1.17 neonates/survivor observed in the control samples. This comparison was made using Fisher's LSD test. Field samples for station CD4 were not tested for sublethal endpoint significance. Station CD3 did not exhibit toxicity contributing to a lower reproduction.

The measurable average amphipod growth rate observed in the field sediment samples was 0.017 and 0.008 for stations CD3 and CD4, respectively. The growth rate for station CD3 was not significantly less than the growth rate of 0.022 mg/day observed in the control samples. This comparison was made using Fisher's LSD test. Field samples for station CD4 were not tested for sublethal endpoint significance. Station CD3 did not exhibit toxicity contributing to a lower reproduction.

Ambient sediment bioassays are only capable of establishing the existence of sediment toxicity, therefore further chemical analyses were required to determine whether As, Cd or Ag contamination were a source of observed sediment toxicity. Bulk sediment chemistry analysis was conducted in order to measure total As, Cd and Ag concentrations within the sediment (Baker, 2004). The sediment concentrations (mg/kg dry weight) and appropriate sediment quality benchmarks are presented in Table 9.

Sediment quality guidelines (SQG's) are used in the absence of sediment quality criteria to predict the likelihood of impacts to sediment biota given a specific contaminant concentration observed in the sediment. Numerous organizations have established SQG's for sediment management and ecological risk assessment purposes. Generally, each guideline consists of two levels: a threshold value below, which effects are improbable or unlikely; and values at or above which impacts are probable or likely. In this analysis, bulk sediment concentrations were compared to various "threshold" SQGs (TEL, ERL, ERM, TEC) to determine the likelihood for a role in the observed toxicity for Ag, As or Cd. The threshold effect concentrations are intended to identify contaminant concentrations below which harmful effects on sediment-dwelling organisms are not expected.

Station	Date	Contaminant	Concentration (mg/kg)	TEL*	ERL*	ERM*	TEC*
CD3	10/1/03	Ag	0.57	0.73	1	3.7	-
CD4	10/1/03	Ag	0.6	0.73	1	3.7	-
CD3	10/1/03	As	7.21	7.24	8.2	70	9.79
CD4	10/1/03	As	9.82	7.24	8.2	70	9.79
CD3	10/1/03	Cd	0.29	0.676	1.2	9.6	0.99
CD4	10/1/03	Cd	0.23	0.676	1.2	9.6	0.99

Table 9: Sediment Concentrations

* SQGs are defined in Appendix A

Cd and Ag concentrations at stations CD3 and CD4 and As concentrations at Station CD3 in bulk sediment are below all of the threshold screening benchmarks listed. Although, the As concentration at station CD4 is only slightly higher than the ERL, TEL, and TEC, the certainty in the SQC's and lack of regulatory applicability combined with very favorable comparisons with more rigorous regulatory water criteria in both the water column and porewater, provide a weight of evidence favoring a determination that the aquatic life use is supported and the toxicity found is due to other substances. Therefore, it is unlikely that the sediment toxicity observed in the 28 day bioassays was due to the presence of As, Cd or Ag at aquatic life-impairing levels.

4.0 CONCLUSION

Based on the water column and sediment samples collected at two monitoring stations in the Back Creek, from March 2003 to October 2003, concentrations of As, Cd and Ag in the sediment and water column are not sufficiently high to impair the aquatic life use for Back Creek. Bottom sediment samples collected and used for bioassay toxicity tests, demonstrate no impacts on amphipod survival at station CD3. A sediment chemistry analysis demonstrated that Ag and Cd concentrations at station CD3 and CD4 and As concentrations at station CD3 in the bulk sediment are all below the threshold screening benchmarks, whereas the As concentration at station CD4 is slightly higher than the ERL, TEL and TEC. A porewater analysis established that As, Cd and Ag concentrations met numeric water quality criterion. Based on these analyses it is unlikely sediment toxicity is due to the presence of As, Cd and Ag. The State will remove As, Cd, and Ag as impairing substances in Back Creek from the 303(d) list, but will relist the segment for aquatic life use impairments due to sediment toxicity (unidentified contaminants) on the 2006 303(d) list. The new listing will be available for public review in the late fall 2005. This will require the State to perform additional studies in this area to identify the contaminant(s) responsible for causing the observed sediment toxicity.

5.0 REFERENCES

Baker, J.E. 2003 Upper Chesapeake Bay Chemical Contaminant Study. University of MD, Chesapeake Biological Laboratory, October 2004.

Coastal Environmental Service, Inc. *Patapsco/Back River Watershed Study*, prepared for the MDE and TARSA, September 30, 1995.

COMAR 26.08.02.03-2G. Numerical Criteria for Toxic Substances in Surface Waters.

COMAR 26.08.02.03-1(B)(3)(g). Toxic Substance Water Quality Criteria for Surface Waters.

COMAR 26.08.02.08(G). Stream Segment Designations.

Fisher, D., Yonkos, L., Ziegler, G., Shepard, M. *Chronic Toxicity of Sediments from the Bohemia River, Elk River, Northeast River and C&D Canal to Leptocheirus plumulosus.* University of MD, Wye Research and Education Center, August, 2004.

SQG - Long, E.R. and Morgan, L.G. *The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program*. NOAA Technical Memorandum. NOS OMA 52. National Oceanic and Atmospheric Administration, Settle, WA. 175 pp. 1991

SQG - MacDonald, D.D, Ingersoll, C.J., and Berger, T. *Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems*. Arch Environ Contam Toxicol 39:20-31. 2000.

Maryland Department of Planning, 2002 Land Use, Land Cover Map Series. 2002.

SQG - Smith, S.L., Macdonald, D.D., Keenleyside, K.A., Ingersoll, C.G. and Field, J. *A preliminary evaluation of sediment quality assessment values for freshwater ecosystems*. J Great Lakes Res, 22:624-638, 1996.

Soil Conservation Service (SCS). Soil Survey of Baltimore County, MD, 1976.

U.S. Environmental Protection Agency. *Methods for Assessing the Chronic Toxicity of Marine and Estuarine Sediment-associated Contaminants with the Amphipod Leptocheirus plumulosus.* EPA-600-R-01-020. First Edition. Office of Research and Development, Washington, D.C. 103 pp. March 2001.

U.S. Environmental Protection Agency. *Consolidated Assessment and Listing Methodology: Toward a Compendium of Best Practices*. 1st edition. July 2002.

U.S. Environmental Protection Agency. National Recommended Water Quality Criteria: 2002.

EPA-822-R-02-047. November 2002.

Appendix A – Sediment Quality Guidelines

ERL - Effects Range Low (Long and Morgan, 1991) is the concentration of a chemical in sediment below which toxic effects are rarely observed among sensitive species.

ERM - *Effects Range Median (Long and Morgan, 1991) is the concentration of a chemical in sediment above which toxic effects are probable among sensitive species.*

TEL - Threshold Effects Limit (Smith et.al. 1996) is calculated as the contaminant concentration value corresponding to the geometric mean of the 15^{th} percentile of the effects data and the 50^{th} percentile of the no-effects data, and generally corresponds to a level where toxicity is not likely.

TEC - Threshold Effects Concentration - Consensus-based (Macdonald et al, 2000): The consensus-based TEC incorporates the Ontario Ministry of the Environment lowest-observed effect levels (LELs): as well as data from up to five other sediment quality guidelines (when available), including TELs, ERLs, TELs for 28 day Hyalella azteca toxicity test, minimal effects thresholds (MET) and chronic equilibrium partitioning thresholds. Consensus-based TECs were calculated by determining the geometric mean of 3 or more of the sediment quality guidelines that were available for a chemical.