

# Update on Toxic Metals Effort in Baltimore Harbor



Maryland Department of the Environment  
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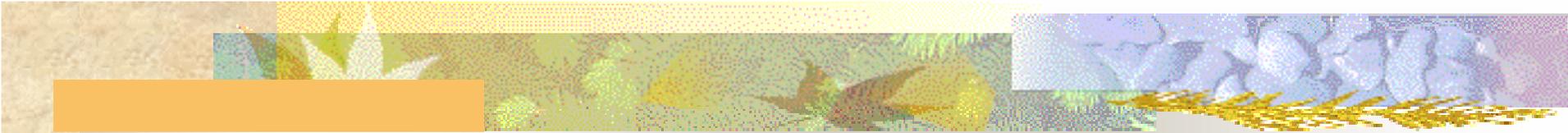
# Presentation Overview

- Review August Sampling Effort in Bear Creek and the Inner Harbor/Northwest Branch
  - Justification, focus, and results
- Shift of sediment based endpoints to water column based endpoints
  - Rationale
- Implications for TMDL process
- Next Steps



# August Sampling Justification

- Stakeholders questioned the Cr impairment
  - Is the Cr present in the sediments of the Inner Harbor and Bear Creek the cause of toxicity?
  - There are significant differences in toxicity between Total Cr, Cr III, and Cr VI
- Stakeholders questioned the endpoint
  - Is the sole use of an ERM-Q value the best TMDL endpoint given the limitations of the ERMs (i.e., guidelines)
- Does the chemistry of the Harbor support the conclusion that Pb, Zn, and Cr in the sediment are the source of toxicity?



# August Sampling Justification

- Based on the stakeholder generated concerns...
  - MDE determined it needed to revisit the sediment-based endpoint. MDE reviewed the most current research and conducted additional monitoring. The results follow:
- The current science indicates the major route of metals exposure is through porewater.
- Scientific studies on Cr III sediment ingestion indicates it is not harmful to benthic organisms
- Scientific studies on Zn and Pb sediment ingestion are insufficient to determine impact.



# August Sampling Focus

- Samples were collected in Bear Creek and the Northwest Branch to evaluate the following:
  - Sediment: Total Metals, Sulfides, Acid Volatile Sulfur – Simultaneously Extracted Metals
  - Water Column & **Porewater**: Dissolved and total metals, Cr was also analyzed for Cr III and Cr VI
  - Toxicity: Acute toxicity test conducted on *L. plumulosus*

# BC and NWB Cr Water Data

Northwest Branch

Freshwater WQS: Cr III = 74ug/L, Cr VI = 11ug/L

Station	Water Column		Porewater	
	Cr (III)	Cr (VI)	Cr (III)	Cr (VI)
	µg/L			
BSM68	0.222	0.279	0.07	ND
BSM69	0.129	0.163	0.31	ND
BSM70	0.125	0.262	0.50	ND
BSM71	0.109	0.131	0.50	ND
BSM73	0.070	0.178	0.36	ND

Bear Creek

Saltwater WQS: Cr III = ?, Cr VI = 50

Station	Water Column		Porewater	
	Cr (III)	Cr (VI)	Cr (III)	Cr (VI)
	µg/L			
BSM28	0.263	0.176	0.05	ND
BSM29*	0.171	0.175	0.12	ND
BSM30	0.355	0.143	0.09	ND
BSM31	0.138	0.168	0.12	ND
BSM32*	0.132	0.148	0.17	ND

In NW Branch and Bear Creek the porewater and water column data are well below criteria

# BC and NWB Zn and Pb Water Data

## Northwest Branch

Freshwater WQS: Zn = 120ug/L, Pb = 2.5ug/L

Station	Water Column		Porewater	
	Zn	Pb	Zn	Pb
	µg/L			
BSM68	20.8	0.053	1.94	0.798
BSM69	24.0	0.134	4.85	1.18
BSM70	23.6	0.036	2.09	1.58
BSM71	29.7	0.108	1.85	1.47
BSM73	20.0	0.044	3.69	0.985

## Bear Creek

Saltwater WQS: Zn = 81ug/L, Pb = 8.1ug.L

Station	Water Column		Porewater	
	Zn	Pb	Zn	Pb
	µg/L			
BSM28	2.25	0.002	1.77	0.685
BSM29*	2.45	0.021	1.20	0.773
BSM30	11.9	0.014	1.56	0.714
BSM31	8.63	0.070	1.54	0.658
BSM32*	8.65	0.086	1.10	0.646

In the NW Branch and Bear Creek the porewater and water column data are well below criteria

# NW Branch Sediment Data

<b>Station</b>	<b>Total Cr</b>	<b>AVS/SEM Cr</b>	<b>Percent SEM</b>
	<b>mg/Kg DW</b>	<b>mg/Kg DW</b>	<b>%</b>
BSM68	443	83	18.8
BSM69	480	110	22.9
BSM70	1,068	243	22.7
BSM71	1,286	343	26.7
BSM73	500	105	20.9
<b>Station</b>	<b>Total Zn</b>	<b>AVS/SEM Zn</b>	<b>Percent SEM</b>
BSM68	661	419	63.4
BSM69	703	434	61.7
BSM70	790	423	53.5
BSM71	970	594	61.3
BSM73	618	389	62.9
<b>Station</b>	<b>Total Pb</b>	<b>AVS/SEM Pb</b>	<b>Percent SEM</b>
BSM68	298	209	70.0
BSM69	352	253	71.8
BSM70	394	227	57.7
BSM71	470	339	72.1
BSM73	312	237	75.8

In the Northwest Branch the fraction of metals associated with the sulfide fraction ranges from 19% - 76%

# Bear Creek Sediment Data

<b>Station</b>	<b>Total Cr</b>	<b>AVS/SEM Cr</b>	<b>Percent SEM</b>
	<b>mg/Kg DW</b>	<b>mg/Kg DW</b>	<b>%</b>
BSM28	705	360	51.0
BSM29	724	322	44.3
BSM30	827	561	67.9
BSM31	847	246	29.0
BSM32	601	312	52.0
<b>Station</b>	<b>Total Zn</b>	<b>AVS/SEM Zn</b>	<b>Percent SEM</b>
BSM28	1530	1120	73.2
BSM29	1930	1253	64.9
BSM30	1870	1820	97.3
BSM31	2230	1170	52.5
BSM32	1490	1160	77.9
<b>Station</b>	<b>Total Pb</b>	<b>AVS/SEM Pb</b>	<b>Percent SEM</b>
BSM28	153	152	99.4
BSM29	276	211	76.7
BSM30	259	297	114
BSM31	247	211	60.7
BSM32	200	184	91.8

In Bear Creek the fraction of the metals associated with the sulfide fraction ranges from 29% - 99%

# Toxicity Data

## Bear Creek

Station	% Survival
Control 1	88
<b>BSM 68</b>	<b>61</b>
<b>BSM 69</b>	<b>35</b>
<b>BSM 70</b>	<b>9.4</b>
<b>BSM 71</b>	<b>3.0</b>
<b>BSM 73</b>	<b>55</b>

## Norwest Branch

Station	% Survival
Control 2	87
<b>BSM 28</b>	<b>0</b>
<b>BSM 29</b>	<b>72</b>
<b>BSM 30</b>	<b>2</b>
<b>BSM 31</b>	<b>80</b>
<b>BSM 32</b>	<b>63</b>

Toxicity was exhibited at all stations except BSM 31



# Use of Water Column Based Endpoints

- Current science indicates
  - Partitioning of a chemical between the sediment and water column/porewater regulates chemical availability
  - Sulfide concentrations regulate metals partitioning
  - Porewater concentrations are more scientifically defensible than total sediment concentrations in the bulk sediment



# Use of Water Column Based Endpoints

- MDE reviewed the Sediment Triad methodology used to list Harbor for Metals
  - The methodology is sufficient to determine impairments
  - However it does not provide the quantitative endpoint needed for TMDL development



# Endpoint Assessment

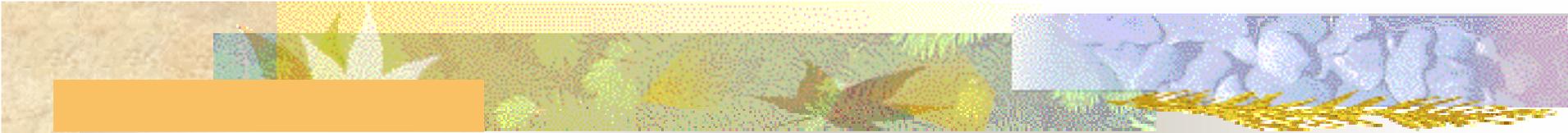
## ■ Endpoint:

- MDE evaluated porewater data against the water column standard to determine if an impairment exists
- Porewater data indicates that water column based water quality standards for Cr, Zn, and Pb are NOT being violated
- Sulfide data indicates that high levels of sulfides are binding metals within the sediments and restricting bioavailability



# Implications on TMDL Process

- MDE is shifting from the ERM-Q sediment based endpoint to an endpoint based on comparing porewater concentrations to water quality criteria
  - This is analogous to evaluating ambient water column data against water column based criteria
- Therefore, based on the updated information:
  - Cr, Pb, and Zn do not appear to be impairing the aquatic life use of the sediment based on porewater concentrations



# Implications on TMDL Process

- Sediment toxicity observed in both the NWB and BC sediments are due to unknown substances and will be investigated in the near future
- The current Cr, Pb, and Zn impairments in the Northwest Branch and Bear Creek will be addressed by Water Quality Analyses and removed as impairing substances from the 2006 303(d) list
- The Harbor and its tributaries will remain on the 2006 303(d) list as impaired for aquatic life use due to sediment toxicity



## Next Steps

- MDE is beginning to develop a study plan to determine cause(s) of the observed sediment toxicity
  - MDE is planning to host a workshop on sediment toxicity issues in January or February 2004 to determine appropriate data to be collected and evaluation tools needed to assess Harbor
- The plan will be completed in Spring 04 and the study will begin in Summer/Fall 04
- Stakeholder input welcome