Comment Response Document

Regarding the Water Quality Analyses for Lead in the Inner Harbor/Northwest Branch and Zinc in the Inner Harbor/Northwest Branch and Bear Creek Portions of Baltimore Harbor in Baltimore City and Baltimore County, Maryland

Introduction

The Maryland Department of the Environment (MDE) has conducted a public review of the proposed Water Quality Analyses (WQAs) of lead in the Inner Harbor/Northwest Branch and zinc in the Inner Harbor/Northwest Branch and Bear Creek portions of Baltimore Harbor. The public comment period was open from June 22, 2004 through July 21, 2004. MDE received three sets of written comments.

Below is a list of commentors, their affiliation, the date comments were submitted, and the numbered references to the comments submitted. In the pages that follow, comments are summarized and listed with MDE's response.

Author	Affiliation	Date	Comment Number
Beth McGee	Chesapeake Bay Foundation	July 21, 2004	1 through 6
Lee Walker Oxenham	Patapsco Riverkeeper	July 21, 2004	7 through 13
Multiple Signatures	Multiple Organizations	July 21, 2004	14 through 18

List of Commentors

Comments and Responses

1. The commenter states that the Water Quality Analysis (WQA) does not account for bioaccumulation as a pathway for contaminant uptake.

Response: Sediment ingestion may be a potential pathway of uptake of contaminants bound to sediment particles. However, the current scientific literature on this topic remains equivocal on the overall impact. The literature indicates that complex geochemical and biological processes influence contaminant bioavailability and possible bioaccumulation and/or toxicity. A study of the process of digestive fluid solubilization and absorption indicates that in various organisms and with various contaminants, either absorption or solubilization may limit contaminant uptake in organisms (1). The extent to which the metals extracted in gut juices may be assimilated is unknown in various species, and iron oxides/organic matter consumed simultaneously in sediments reduces metal bioavailability (2). It also appears that Zn uptake may be regulated in some species at high concentrations (3). The bioavailability of metals also has been shown to decrease with increased contact time with sulfidic sediments (4).

Due to the highly variable and complex nature of the issue of contaminant bioavailability and bioaccumulation MDE is funding a study that will investigate the potential bioavailability and possible bioaccumulation of contaminants from Baltimore Harbor sediments by the amphipod *Leptocheirus plumulosus* and the polychaete *Nereis virens*. Data from these

investigations will inform us whether sediment contaminants are accumulated, and whether the bioaccumulation is causing toxicity (acute and/or chronic). Toxicity would be the combined effects of exposure to accumulated residues from sediment ingestion and exposure to pore water.

A significant factor affecting the influence of Pb and Zn on sediment toxicity is that a large percentage (approximately 70%) of Pb and Zn found within Baltimore Harbor sediments are bound into metallic sulfide compounds. As stated above, the sulfide-modulated redox status of these metals may also reduce their bioavailability and subsequent accumulation and/or toxicity (4). The current reduction/oxidation conditions within Bear Creek and the Northwest Branch/Inner Harbor produces high levels of sulfides that react with divalent metals, including Pb and Zn. Based on the Acid Volatile Sulfide/Simultaneously Extracted Metals AVS/SEM data, there are significant amounts of excess sulfides throughout the impaired segments.

2. The commenter states that the extraction of porewater may be too 'coarse' of an assessment technique to accurately assess the bioavailability of contaminants to benthic organisms.

Response: MDE is attempting to use the most advanced scientific methods available to develop an accurate assessment of the Baltimore Harbor. The ability to monitor the microenvironment surrounding an amphipod is an extremely difficult task and conducting a scientifically valid field study of microhabitats is not consistent with the broader scale planning effort represented by an impairment listing and TMDL. The toxicity investigation currently underway will significantly expand the understanding of the causes of toxicity within in the Harbor. However, the budgetary constraints in which MDE is operating within do not allow for research on the effects of microhabitats on toxicity. MDE cannot justify further expanding this study to assess this topic, which is a scientific rather than a management issue.

3. The commenter states that nickel is also a Simultaneously Extracted Metal (SEM) and was not analyzed in the MDE chemical analysis. Therefore, the SEM concentrations used in the analysis are underestimated.

Response: Based on data collected during the Baltimore Harbor Sediment Mapping Study (1997), nickel concentrations ranged between $37.7 - 83.2 \,\mu$ g/g dry weight at the Inner Harbor/Northwest Branch stations and $58.7 - 85.9 \,\mu$ g/g dry weight at the Bear Creek stations. The current nickel concentrations in the impaired regions estimated using these data, indicate that nickel increases the value of SEM metals, but not to a level where it significantly affects the sediment chemistry in these regions. Therefore, MDE acknowledges that the SEM concentrations of metals are slightly underestimated without the inclusion of nickel in the data analysis. However, because this underestimation does not fundamentally alter the results of the analysis, MDE will not act any further regarding this issue.

4. The commenter states that synergistic or additive effects of contaminants are not considered, nor are chronic effects/exposures.

Response: MDE is considering Pb and Zn specifically as independent impairing substances; therefore, unless there is direct evidence that either Pb or Zn is directly contributing to synergistic or additive effects, the relevance to the contemplated action is not clear. Further, the toxicity identification study will help to determine whether toxicity may be due to the cumulative impact of several substances, if no single substance is implicated as the cause of the impairment. In fact, additive effects support MDE's action of a biological listing which addresses this issue, pending completion of a toxicity identification study to partition the impact among the multiple contaminants present. The study design (simultaneous assessment of tissue residue and toxicity) may aid in the elucidation of additive or synergistic effects.

The development of TMDLs requires that a specific causative agent be identified as the impairing substance. Based on the most recent data collected, Pb and Zn concentrations in the porewater do not exceed the water column based water quality criteria. Additionally, the absence of sediment criteria deprives the agency of an objective, legally defensible method to evaluate water quality based on contaminant concentrations. During the evaluation process that resulted in the Harbor and its segments being listed as impaired, contaminant additivity was not taken into consideration except by the biological impairment. Therefore, sediment contaminant levels were assessed at stations that exhibited toxicity. The result was that segments were listed as impaired based on observed toxicity and frequency and magnitude of contaminant concentrations that exceeded "state of the science" guidelines (ERMs) at the time, and were utilized to indicate **likely** impairing substances. However, subsequent scientific research has determined that an assessment of bulk sediment concentrations is not the correct approach for determining impairing substances (5).

MDE is attempting to correct this through the process initiated by the Pb and Zn WQA. The first step in this process has been to determine that no water quality criteria is being violated by the specific contaminants listed as an impairing substance. Upon completion of the WQA process, MDE will maintain the Baltimore Harbor as impaired by sediment toxicity but without specific impairing substances. The study MDE is currently conducting and referenced by the commenter in the formal comments will investigate the potential contaminant interactions through concomitant analysis of benthos tissue residues and acute or chronic toxicity endpoints. The goal of this study is to address the uncertainty of the original water quality assessment that resulted in the listing of specific contaminants (including Pb and Zn) as impairing substances without sufficient direct data supporting the conclusion. Once the investigations are complete (expected completion date is December 2005) MDE will utilize the current studies to move forward to determine the impairing substance(s) and TMDL development.

5. The commenter states that using porewater as a surrogate to evaluate sediment toxicity is not consistent with the current scientific thinking on sediment Toxicity Identification and Evaluations and recommends that any decisions regarding the cause of toxicity be reserved until the completion of the stressor identification study.

Response: This comment relates back to the first comment. The assumption is that if water quality standards are met, there will be no toxicity. This assumption is challenged in

sediments by an additional route of ingestion. MDE chose to evaluate porewater concentrations against water column criteria because this method is consistent with Clean Water Act guidance that states that data used to conduct a WQA needs to be of similar quality and level of specificity as that data used to list waterbodies as impaired. Since the listings for Pb and Zn were not based on water quality criteria, rather a co-occurrence based threshold, MDE is complying with the Act by utilizing the assessment of potential toxicity using porewater compared against the appropriate water quality criteria. The planned study will incorporate the current thinking on conducting more in-depth toxicity evaluations in such complex systems.

MDE is planning to remove references to Pb and Zn as specific impairing substances from the listing for Baltimore Harbor because the best current science does not demonstrate that they are causing the observed toxicity. The Harbor remains on Maryland's 303(d) list due to observed toxicity. The present decision does not preclude the inclusion of these same specific substances on the list if conclusions of the toxicity identification study support the decision.

6. The commenter states that the proposed action is inconsistent with commitments made by the state to clean-up Baltimore Harbor and that the decision was made without input from the Baltimore Harbor Stakeholder Advisory Group.

Response: The proposed action is not inconsistent with previous commitments. This WQA is meant to address an inadequate assessment of conditions previously conducted by MDE and addressed in the response to Comment 4. The actions currently undertaken by MDE are meant to ensure that the management decisions taken to improve water quality within the Baltimore Harbor are scientifically justifiable and will result in improvements in the Baltimore Harbor ecosystem.

The Baltimore Harbor Stakeholder Advisory Group (SAG) initiated the process that led to the development of this WQA. It was members of the SAG that questioned the previous assessment of Baltimore Harbor data and the use of an Effects Range Mean Quotient (ERM-Q) sediment endpoint. Based on these concerns MDE proposed further research to collect porewater data. The porewater collection effort was discussed during the July 29, 2003 SAG meeting. MDE indicated the data collected during the study would be used to reassess the chromium impairment in the Harbor. During the meeting no significant objection was raised with this approach.

Subsequently, a literature review was conducted on divalent metals toxicity pathways. Based upon the results of the literature review and the need for consistent assessment methods, MDE determined that assessing porewater against water column based water quality criteria provides MDE with objective, legally defensible water quality endpoints for the contaminants of concern within Baltimore Harbor. Based on this assessment, the contaminants of concern are not impairing water quality. As a result, MDE decided to complete WQA's for the contaminants of concern and subsequently conduct further studies to identify the causes of toxicity within the Harbor. Based on this decision, MDE sought out and received substitutive input from the SAG in developing the current toxicity identification

study. Based on this input throughout the process, MDE feels that the SAG has been an intricate part of the process.

7. The commenter questions where is the 'model' and 'roadmap' to address the impacts of toxics on water quality in the Baltimore Harbor.

Response: The highly complex nature of the Baltimore Harbor requires MDE to utilize an adaptive management approach. MDE has spent, and continues to spend, significant resources on assessing the conditions of the Harbor and developing management approaches to improve water quality of this highly urbanized environment. MDE is committed to this effort and continues to work towards its success. However, the complex nature of the problem requires MDE to consider a significant amount of information in developing management approaches. To this end, the current MDE approach to improving water quality in Baltimore Harbor is centered on: 1) maintaining the Harbor impairment for toxicity on the 303(d) list, 2) investigating the source of toxicity, 3) using the data from the investigation to identify possible impairing substances that will require TMDLs, and 4) removing substances from the 303(d) list that cannot be proven as impairing substances.

To investigate and address the sediment toxicity impairment, MDE is conducting a field study scheduled to begin in September 2004 and be completed by December 2005. The goal of the study is to identify the substance or substances that are causing the sediment toxicity observed in the Harbor and address the potential that sediment ingestion could be a route of exposure. Information on the study can be attained from MDE upon request by contacting the TMDL outreach staff at 410-537-3902. Once the study is completed, MDE will utilize the information to begin developing TMDLs for the compound or compounds identified as causes of toxicity.

8. The commenter suggests that the WQA is a step backward and questions why TMDLs are not being developed if the water body does not meet water quality standards.

Response: The approach MDE is undertaking is consistent with protecting water quality under the Clean Water Act. Under the requirements of the Act, both the Northwest Branch/Inner Harbor and Bear Creek will remain on the 303(d) list as impaired due to sediment toxicity. This listing will continue to require MDE to address the impairment. However, the Clean Water Act also states that a segment identified as a WQLS may not require the development 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 the criteria; 3) refinements to water quality criteria, or the interpretation of those standards, which result in criteria being met; or 4) correction to errors made in the initial listing.

The water quality analysis for Pb and Zn considers factor 1) in that more recent data (porewater analysis) indicates that the specific impairing substances do not exceed regulatory criteria, and 4) that the attribution of 'impairing substance' to either Pb or Zn in the respective locations was based on an inappropriate linkage of sediment Pb and Zn concentrations to sediment toxicity.

In the absence of sediment quality criteria, MDE has elected to utilize an analysis of porewater concentrations against water quality criteria to determine if a water column impairments exist. Based on the assessment of Pb and Zn porewater data versus their respective water quality standards, neither Pb nor Zn violates water quality standards and therefore cannot be identified as an impairing substance.

9. The commenter suggests that the WQA is "effectively denying the Patapsco River the protections promised by the Clean Water Act" and questions the information used to make the decision to complete the WQA. Additionally, the commenter states that the data used in the WQA does not show any reduction in the impairment and that the data reveal the sediment toxicity to be similar to previous measurements.

Response: The toxicity data assessed in the WQA indicates that sediment toxicity in the impaired segments has not decreased. As a result the segments will remain impaired for toxicity. However, the porewater data indicates that neither Pb nor Zn are at concentrations sufficient to cause the observed toxicity or violate water quality standards.

10. The commenter suggests that MDE used porewater concentrations to assess toxicity and that this method is not sufficient to estimate what is bioavailable to sediment organisms.

Response: See response to Comment 5

11. The commenter indicates that by conducting the study to investigate the sources of toxicity in Baltimore Harbor sediments, MDE acknowledges that porewater data is insufficient to produce reliable conclusions.

Response: The comment is not valid in that the porewater analysis did not consider many possible causes of toxicity, especially organic compounds. The porewater analysis conducted by MDE produced reliable data on what metals were present in the water column, thereby allowing MDE to assess whether or not a particular metal was violating water quality standards. The toxicity identification study that MDE is sponsoring will produce more comprehensive results that will allow an assessment of the groups of contaminants that may be contributing to the observed sediment toxicity.

12. The commenter suggests that it would be prudent for MDE to wait until the conclusion of the current toxicity identification study prior to making decisions regarding the 'source, nature, or degree of toxicity of the toxic contaminants in Baltimore Harbor'.

Response: MDE is planning to remove references to Pb and Zn as specific impairing substances from the listing for Baltimore Harbor because the best current science does not

demonstrate that they are causing the observed toxicity. The Harbor remains on Maryland's 303(d) list due to observed toxicity. The present decision does not preclude the inclusion of these same specific substances on the list if conclusions of the toxicity identification study support the decision.

13. The commenter suggests that the WQA is a step backwards in trying to address the impairments within the Patapsco River and violates the comprehensive pollution control program Congress established with the Clean Water Act.

Response: MDE does not feel that the WQA is a step backwards nor does it violate the Clean Water Act. The WQA is the result of a more recent analysis that indicates that previous efforts to assess the Harbor were incomplete. The goal at MDE is to continue forward with assessing and addressing the impairments in a manner that will allow management decisions to be developed that will address the causes of sediment toxicity.

14. The commenter indicates that the MDE decision is premature, based on inadequate science, and suggests that MDE should "focus their efforts on correcting the toxicity problems in the Harbor, instead of these proposals to 'de-list' it".

Response: MDE feels that the effort used to assess the Northwest Branch/Inner Harbor and Bear Creek is consistent with EPA guidance that requires data used in a WQA to be sufficiently comparable to the data used to list the segment as impaired. Based on this information neither Pb nor Zn violates water quality standards in the water column. Additionally, the *in situ* sediment chemistry indicates that a significant majority of Pb and Zn is converted to non-toxic forms that are sequestered in the sediments.

MDE also feels that this effort is not contrary to previous efforts made to improve water quality in Baltimore Harbor. The previous listings of Pb and Zn were based on toxicity results and bulk sediment concentrations. The method to assess the impacts of metals in estuaries has improved. This WQA reflects the improvement in the assessment science. MDE remains committed to improving water quality within the Harbor and is currently undertaking a study to investigate the source of the observed sediment toxicity. Upon completion of this study MDE will move forward with an effort to develop TMDLs for the substance(s) identified as a cause of the toxicity.

15. The commenter suggests that the porewater approach does not factor in bioaccumulation as a source of toxicity.

Response: See response for Comment 1.

16. The commenter recommends that decisions regarding the cause(s) of sediment toxicity in Baltimore Harbor be reserved until the current study is completed.

Response: See response for Comment 12.

17. The commenter suggests that more needs to be done to reduce and eliminate toxic chemicals from entering Baltimore Harbor and believes the WQA weakens MDE's authority and ability to require much needed load reductions.

Response: MDE regulates the point source community contribution via the NPDES permit process. Over the course of the past 30 years this program has successfully helped to reduce the load of toxic chemicals entering Baltimore Harbor significantly. MDE also regulates Anne Arundel County, Baltimore City and Baltimore County via the Municipal Separate Storm System (MS4) NPDES permit process. These permit-based programs will not be relaxed based on this WQA. MDE is seeking to identify the source(s) of the toxicity in the Harbor so that appropriate management decisions can be made that will improve the water quality of the Harbor. Although Pb and Zn sediment geochemistry provides conditions that mitigate the effect of Pb and Zn on biota. Based on the best available management level science, this action is not contrary to actions that will improve water quality in the Harbor. Additionally, this action will not weaken MDE's statutory ability to require appropriate load reductions in the future when the sources of toxicity are identified.

18. The commenter suggests that the proposed action runs counter to the good faith effort made by many members of the Baltimore Harbor Stakeholder Advisory Group.

Response: See response for comment 6.

References

- 1. Weston, Donald, P., Sediment Extraction Using Deposit-Feeder Gut Fluids: A Potential Rapid tool for Assessing Bioaccumulation Potential for Sediment Associated Contaminants, US Army Corps of Engineers, ERDC/EL TR-02-18, 2002.
- 2. Fan, Wehhong and Wang, Wen-Xiong, Sediment Geochemical Controls on Cd, Cr, and Zn Assimilation by the Clam *Ruditapes Philippinarum*., Environmental Toxicology and Chemistry, Volume 20, No. 10, pp. 2309-2317, 2001.
- 3. Yan, Qi-Lun and Wang, Wen-Xiong, Metal Exposure and bioavailability to a Marine Deposit-Feeding Sipuncula, *Sipunculus nudus*. Environmental Science and Technology, Volume 36, Number 1, 2002.
- 4. Griscom, Sarah B., et. al., Geochemical Influences on Assimilation of Sediment Bound Metals in Clams and Mussels. Environmental Science and Technology, Volume 34, pages 91-99. 2000.
- 5. Lee, G.F. and Jones-Lee, A., Unreliability of Sediment Co-Occurrence-Based Approaches for Evaluating Aquatic Sediment Quality, 2003. Excerpted from
 - a. Lee, G.F. and Jones-Lee, A. Organochlorine Pesticide, PCB and Dioxin/Furan Excessive Bioaccumulation Management Guidance, California Water Institute Report TP02-06 to the California Water Resources Control Board/Central Valley Regional Water Quality Control Board, California State University Fresno, CA