

Final

Comment Response Document Regarding the Water Quality Analyses for Chromium 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 chromium in the Inner Harbor/Northwest Branch and Bear Creek portions of Baltimore Harbor. The public comment period was open from May 10, 2004 through June 8, 2004. MDE received five 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.

List of Commentors

Author	Affiliation	Date	Comment Number
Beth McGee	Chesapeake Bay Foundation	June 7, 2004	1 through 5
Sherry Krest	US Fish and Wildlife Service	June 8, 2004	6 through 9
Lee Walker Oxenham	Patapsco Riverkeeper	June 8, 2004	10 through 17
Multiple Signatures	Multiple Organizations	June 8, 2004	18 through 22
Michael Powell	Honeywell Inc.	May 28, 2004	23 through 28

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. Assimilation efficiency and efflux rates of contaminants have been shown to vary widely based on contaminant, test species, testing regime, and environmental conditions (1). The bioavailability of metals also has been shown to decrease with increased contact time with sulfidic sediments (2). Also, the geochemistry of chromium VI (Cr VI) in anoxic sediments containing sulfur compounds results in the oxidation of sulfides and the concomitant reduction of Cr VI to Cr III (3). A study of the process of digestive fluid solubilization and absorption indicated that absorption might limit contaminant uptake in organisms. That is, contaminants may be solubilized in an organisms gut but not absorbed into the organism. For example, a digesting fluid extraction study in the bivalve *Macoma nasuta* indicated that although Cr III was solubilized, it was not absorbed (4).

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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*. Bioaccumulation will tell us whether contaminants are accumulated or whether bioaccumulation is causing toxicity. Toxicity would be the combined effects of accumulated residues from sediment and possible pore water toxicity.

A significant factor affecting the influence of Cr on sediment toxicity is that the large majority of Cr found within Baltimore Harbor sediments is trivalent Cr or Cr III. The current reduction/oxidation conditions within Bear Creek and the Northwest Branch/Inner Harbor produces high levels of sulfides that will convert the more toxic Cr VI to the less or non-toxic Cr III. Due to the lack of toxicity, EPA has not established water quality criteria for Cr III. Additionally, the EPA Atlantic Ecology Division has conducted research on Cr III that indicates that Cr III does not exhibit toxicity at levels well above the Effects Range Median (4,5). Therefore, even if sediment ingestion is a pathway of exposure to contaminants, the Cr that organisms would be exposed to would be Cr III, a substance shown to exhibit little potential toxic impact.

Finally, EPA developed sediment quality criteria for several organic compounds utilizing the equilibrium partition approach. Based on EPA's support of this theory, MDE feels it is consistent with the EPA approach to assessing the impairment.

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. Additionally, the thermodynamics that govern the conversion of Cr III to Cr VI in sediments is slow, and significant oxidation of Cr III to Cr VI occurs only in soils and sediments with elevated concentrations of manganese oxides and low organic content (3). The toxicity investigation currently underway will significantly expand the understanding of the causes of toxicity within the Harbor. However, the budgetary constraints in which MDE is operating within does 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 the presentation of Cr data in a molar format is not appropriate because it does not act like a SEM metal by forming an insoluble metal sulfide.

Response: The molar presentation has utility in the analysis of the sediment chemistry data because it highlights that there is an excess of acid volatile sulfides (AVS) in the sediments of the Baltimore Harbor. The excess AVS indicates that reducing conditions are present

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within the sediments and that under these conditions; the Cr present in the sediment will be Cr III (Berry personal communication 2004). As such, the risk of toxicity is significantly reduced, if not eliminated. Therefore, a molar analysis is applicable to the assessment of the sediment chemistry data as it indicates the level of oxidation/reduction possible in the sediments. However, because Cr does not act like a SEM, forming a metal sulfide, the language in the water quality analysis referring to the potential binding of Cr III with the excess sulfides will be removed from Section 3.2, Sediment Chemistry Analysis.

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

Response: MDE is considering chromium specifically as an impairing substance; therefore unless there is direct evidence that chromium is a direct contributor to synergistic or additive effects, the relevance to the contemplated action is not clear. Further, the study that is planned 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.

The development of TMDLs requires that a specific causative agent be identified as the impairing substance. Based on the most recent data collected, Cr VI concentrations in the porewater are two (2) orders of magnitude lower than the water column based water quality criteria. Additionally, the absence of sediment criteria does not provide the agency 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. 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 contaminant concentrations were used only to indicate likely impairing substances. However, subsequent scientific research has determined that bulk sediment concentrations are not the correct approach for determining impairing substances.

MDE is attempting to correct this through the process initiated by the Cr WQA. The first step in this process has been to determine that no water quality criteria is being violated by the specific contaminant listed as an impairing substance. Upon completion of the WQA process, MDE will maintain the Baltimore Harbor as impaired for toxicity but without specific impairing substances. The study MDE is currently conducting and referenced by the commenter in the formal comments will investigate the synergistic/additive or chronic effects of contaminants on sediment toxicity. The goal of this study is to address the weakness of the previous assessment that resulted in the listing of specific contaminants as impairing substances without sufficient direct data supporting the conclusion. Once the study is completed (expected completion date is December 2005) MDE will move forward with determining the impairing substance(s) and developing TMDLs.

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.

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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, however, it should be noted that any ingested contaminated particulate material in the water column would have been included in development of the criterion. The use of porewater concentrations evaluated against water column criteria has been chosen by MDE as a method that maintains consistency with Clean Water Act guidance that states that data used to conduct a WQA needs to be of sufficient quality and level of specificity as that data used to list waterbodies as impaired. Within Maryland, MDE has chosen this method to be consistent with this guidance when assessing impairments due to toxic contaminants. The planned study will incorporate the current thinking on conducting more in-depth toxicity evaluations in such complex systems.

6. The commenter states that the bioavailability and toxicity of chromium is likely to flux seasonally and during dramatic weather changes and questions whether the data used in the analysis is representative of conditions in the Harbor because the samples used in the WQA were collected during August and during an above average rainfall year.

Response: The impacts of seasonal and weather derived changes in the ecosystem do not result in large changes in the oxidation rate of Cr III to Cr VI. The oxidation of Cr III to Cr VI is slow (i.e., months) (6). Therefore, short-term seasonal changes affecting reduction/oxidation states at the sediment water interface do not increase the amount of Cr VI present in sediment. Additionally, the high levels of AVS present in Harbor sediments are indicative of an environment that is not conducive to the oxygenation of Cr III to Cr VI. Although the samples were collected during a wet year and during the time of year when dissolved oxygen levels are low, the in situ sediment chemistry will maintain an environment that will not vary significantly enough to consider the samples unrepresentative.

7. The commenter states that other metals work synergistically with chromium to cause toxicity and that this relationship should be considered before removing chromium as an impairing substance.

Response: See response to Comment 4.

8. The commenter states that using porewater and water column concentrations of speciated chromium are an appropriate indicator of toxicity is a matter of some debate.

Response: See response to Comment 5.

9. The commenter states that assessing chromium through water exposure alone is only a portion of the risk posed to aquatic life and suggests that food chain modeling is needed to rule out risks to piscivorous birds and mammals.

Response: MDE feels that it is unnecessary to conduct a food web model to rule out impacts to fish and mammals. Based on the information provided by EPA there is no significant biomagnification of chromium in aquatic food webs (7). The toxic effects of chromium are primarily found at the lower trophic levels. Chromium may bioaccumulate in algae, other

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aquatic vegetation, and invertebrates, but it does not biomagnify. Given MDE's resources, and the need to complete TMDLs in a timely manner, a food web model is not appropriate for a substance that does not biomagnify.

10. The commenter questioned the MDE approach for prioritizing and developing a 'roadmap' to address the water quality issues and develop TMDLs for 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.

11. The commenter suggests that the WQA 'effectively denies the Patapsco River the protections promised by the Clean Water Act' and questioned on what basis the decision to remove Cr as an impairing substance was reached.

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 Cr 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 Cr in the respective locations was based on an inappropriate linkage of sediment Cr 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 water column impairments exist. Based on the assessment of Cr porewater data versus the water quality

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standard, Cr does not violate water quality standards and therefore cannot be identified as an impairing substance.

12. The commenter states that the data used in the WQA do not show any reduction in impairment and that the data reveal the 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 Cr is not at a concentration sufficient to cause the observed toxicity or violate water quality standards.

13. 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

14. The commenter suggests that sediment ingestion is not taken into account during this analysis.

Response: See response to Comment 1

15. 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: This conclusion is not valid in that 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 Evaluation 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.

16. The commenter states that ‘the data indicates that the impairment exists, and the extent of the impairment is such that Baltimore Harbor is in the top 1% of waterbodies nationwide, it is unconscionable for the state to remove the river’s protections.’

Response: Assessments of bulk sediment concentrations of metals (including Cr) as an indication of impact on an ecosystem is **not appropriate** in complex urban environments with multiple contaminants and high sulfide levels. The sediment geochemistry is extremely complex and does not allow for direct correlation between concentrations and impact. Furthermore, the Clean Water Act requires that TMDLs be developed for specific substances that are shown to be impairing water quality, however at this time Cr cannot be identified as a source of toxicity for the reasons discussed in the WQA. Lastly, MDE is not removing any protection from the Harbor or it’s impaired segments. MDE is attempting to systematically

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use the most advanced science available for management-based decision making to assess and address the impairments within the Harbor.

17. The commenter suggests that the Cr 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.

18. The commenter indicates that the MDE decision is premature, based on inadequate science, and runs counter to previous commitments to clean up Baltimore Harbor

Response: MDE feels that the effort 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 Cr does not violate water quality standards in the water column. Additionally, the *in situ* sediment chemistry indicates that Cr is converted to a non-toxic form that is 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 listing of Cr was 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.

19. The commenter suggests it would be prudent to wait for the results of the current study prior to making regulatory decisions, including the de-listing of these segments.

Response: The decision to de-list does not preclude MDE from re-listing the Harbor or its segments in the future. The action of de-listing these segments is based on current science. The results of the current study will not be available for approximately one and a half years. MDE has chosen to move forward with this effort prior to the completion of the study while acknowledging that the information gained may result in segments being re-listed. However, at the current time, MDE does not have data to support the listing of Cr as an impairing substance.

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

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Response: See response for Comment 1.

21. 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 19.

22. The commenter suggests that more needs to be done to reduce and eliminate toxic chemicals from entering Baltimore Harbor and believes the WQA runs counter to this effort.

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. Through this process, MDE is ensuring that local jurisdictions implement best management practices that result in reduced loadings of toxic chemicals via the stormwater system. These permit based programs will not be relaxed based this WQA. MDE is seeking to identify the appropriate source(s) of the toxicity in the Harbor so that appropriate management decisions can be made that will affect the water quality of the Harbor. Although Cr sediment concentrations are high relative to other areas of the Chesapeake Bay, the in situ sediment geochemistry provides conditions that mitigate the effect of Cr on biota. Therefore, based on the best available management level science, MDE does not feel this action is contrary to actions that will improve water quality in the Harbor.

23. The commenter indicates that they concur with the MDE decision to utilize porewater concentrations compared against water quality criteria as a analogous to comparing water column data to water quality criteria.

Response: MDE concurs with the commenter.

24. The commenter indicates that the MDE shift of endpoints from sediment guidelines to water quality criteria is legitimate due to the current science that indicates total Cr sediment concentration is not a valid metric for assessing the impact of Cr in sediments.

Response: MDE concurs with the essence of the statement that evaluating total Cr sediment concentrations is not a valid metric for assessing the impact of Cr in sediments due the variation in toxicity associated with Cr III and Cr VI.

25. The commenter supports MDE's rationale of focusing on Cr VI when assessing impairments in waterbodies with Cr.

Response: MDE feels the use of Cr VI valid due to the variations in solubility and toxicity associated with Cr III and Cr VI.

26. The commenter concurs with the MDE conclusion found in Section 4.0 of the WQA.

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Response: NA.

27. The commenter agrees that the WQA should be used to support the removal of the Northwest Branch/Inner Harbor and Bear Creek for Cr from the Maryland list of water quality limited segments when MDE updates the 303(d) list in the future.

Response: MDE will not remove the waterbodies from the list of impaired segments, however Cr will be removed as the impairing substance. The agency does reserve the right to re-list the waterbodies in the future if such data becomes available that indicates Cr is an impairing substance.

28. The commenter suggests that MDE's future plans to assess toxicity should focus on the collection and analysis of porewater and water column data.

Response: MDE will continue to collect porewater data in the Baltimore Harbor to assess if any contaminants violate water quality criteria. However, MDE will also collect additional data as it determines necessary to provide a comprehensive assessment of the sources of toxicity.

References

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