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Methodology for Determining Impaired Waters By Chemical Contaminants for Maryland's Integrated Report of Surface Water Quality

Water & Science Administration
Maryland Department of the Environment

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BACKGROUND

The designated uses define the water quality goals of a water body. At a minimum, the Maryland Department of the Environment (MDE) must provide water quality for the protection and propagation of fish, shellfish, and wildlife, and provide for recreation in and on the water, where attainable (CWA Section 101(a)(2)). The MDE is required to adopt water quality criteria that protect designated uses. Such criteria must be based on sound scientific rationale, must contain sufficient parameters to protect the designated uses, and can be expressed in either numeric or narrative form. Narrative criteria are descriptions of the conditions necessary for a water body to attain its designated use, while numeric criteria are concentration values deemed necessary to protect designated uses. Narrative criteria can be used to assess water quality, and also to establish pollutant-specific discharge limits where there are no numeric criteria or where such criteria are not sufficient to protect the designated use.

Although several approaches exist to assess water quality (e.g. numeric criteria, whole effluent toxicity (WET), etc.), few approaches exist to assess sediment quality due to its complexities. Nevertheless, sediments are an integral component of aquatic ecosystems, providing habitat, feeding, spawning, and rearing areas for many aquatic organisms and are, therefore, protected under the narrative criteria. Furthermore, sediment quality can affect whether or not waters are attaining designated uses. Consequently, it is necessary and appropriate to assess and protect sediment quality, as an essential component of the total aquatic environment, to achieve and maintain designated uses. The difficulty lies in implementing the narrative criteria, which is qualitative in nature. To circumvent this obstacle, MDE is implementing an approach to quantitatively interpret narrative criteria statements, and determine water quality standard violations from contaminated sediments.

INTRODUCTION

Under Section 303(d)(1) of the federal Clean Water Act (CWA), the MDE is required to establish Total Maximum Daily Loads (TMDLs) for those water body segments that do not meet applicable water quality standards and are therefore considered “impaired”. To achieve this, MDE is required to consider all existing and readily available water quality data and information, and develop methods to interpret this data for each potential impairing substance (e.g., pH, nutrient, fecal coliform, etc.).

Even though the Department will adhere to the methods outlined below as closely as possible, there may be instances where our determinations may vary based on scientifically defensible decisions. It is important to note that there may be situations that do not support an impairment determination from chemical contaminants, but rather from another stressor (e.g. dissolved oxygen, pH), and would therefore be addressed elsewhere. This document provides the specific methodology used by MDE for identifying water body segments impaired due to chemical contaminants.

It is not the intent of this methodology to include waters that do not meet water quality criteria solely due to natural conditions or physical alterations of the waterbody not related to anthropogenic pollutants. Similarly, it is not the intent of this chapter to include waters where designated uses are being met and where water quality criteria exceedances are limited to those parameters for which permitted mixing zones or other moderating provisions (such as site-specific alternative criteria) are in effect. The Department will examine these situations on a case-by-case basis, and evaluate the context under which the exceedance exists. Determination of compliance with water quality criteria may be facilitated through special analyses (e.g. normalization of metals to common reference element to determine anthropogenic influences), or monitoring (e.g. compliance monitoring for mixing zones).

MDE considers all existing readily available chemical, toxicological, and biological data from water column, sediments, and fish tissue in determining if a water body segment should be classified as impaired due to chemical contaminants and listed on Category 5 of the Integrated Report. As a result, MDE has divided the impairment evaluation process into three media categories (Water Column, Sediment, and Fish Tissue). The Department will evaluate the Monitoring Plans, Quality Assurance, and Quality Control programs of data providers, and will use best professional judgment to include/exclude data where documentation does not exist.

WATER COLUMN

Ambient water column contaminant data are screened against numerical ambient water quality criteria if available. These water quality criteria are utilized because they represent science-based threshold effect values and are an integral part of the Maryland's water quality standards program. These criteria are divided into the following categories that directly relate to Maryland's surface water use designation classification (COMAR 26.08.02):

All surface waters of the State (USE DESIGNATIONS - I, II, III, & IV)

- Criteria for the protection of aquatic life
  - Fresh water (Chronic & Acute)
  - Saltwater (Chronic & Acute)
- Criteria for the protection of human health from fish tissue consumption (Organism Only)

Surface waters used for public water supply (USE DESIGNATION - P)

- Criteria for the protection of human health from fish tissue consumption & drinking water (Water + Organism)
- Drinking water only (Maximum Contaminant Levels-MCLs)

The water column assessment methodologies using human health criteria and aquatic life criteria will be addressed separately below.

PROTECTION OF HUMAN HEALTH FROM FISH TISSUE CONSUMPTION, DRINKING WATER, AND FISH TISSUE CONSUMPTION PLUS DRINKING WATER

For the assessment of human health endpoints using water column data, EPA provided the following recommendation in the Consolidated Assessment and Listing Methodology (CALM) (EPA 2002) guidance document:

> "*Water quality criteria to protect human health are generally based on protecting against long-term exposure to low concentrations of a toxic pollutant. When a chemical human health criterion is applied to water quality standards attainment decisions, EPA recommends evaluating comparing the mean (or geometric mean if appropriate for a skewed data set) of the measured concentrations with the criterion. However, some states have adopted human-health-based chemical criteria that establish instantaneous maximum concentrations, for which any exceedance constitutes nonattainment. If the mean or geometric mean exceeds the criterion, the WQS is not being attained.*"

Based on this guidance and the fact that Maryland's human health criteria have been developed to address long-term exposure scenarios, Maryland will compare a mean of water column data to the applicable human health criterion when making assessments for the Integrated Report. If the mean exceeds the applicable criterion, that water body will be listed as impaired on Category 5. To ensure that the mean is reflective of ongoing water quality conditions, Maryland will collect and assess a minimum of 10 samples collected over a representative temporal period and spatial extent. MDE will use its best professional judgment to evaluate data with overwhelming evidence of impairment or attainment but fewer than 10 samples. Assessment status in these smaller datasets will be based on the magnitude and timing of any exceedances.

AQUATIC LIFE

Aquatic life water quality criteria are composed of three components: magnitude, frequency and duration. EPA (1985) provides guidance regarding the calculation of the magnitude component as well as the interpretation of the frequency and duration components of acute and chronic aquatic life criteria. The magnitude of acute criteria (also known as the Criteria Maximum Concentration or CMC) is not to be exceeded based on a one-hour average more than once every three years. When discussing the CMC duration component, EPA (1985) states:

> *One hour is probably an appropriate averaging period because high concentrations of some materials can cause death in one to three hours. Even when organisms do not die within the first hour or so, it is not known how many might have died due to delayed effects of this short of an exposure. Thus it is not appropriate to allow concentrations above the CMC to exist for as long as one hour (page-5).*

Furthermore, the magnitude of chronic criteria (also known as the Criterion Continuous Concentration or CCC) is not to be exceeded based on a four-day average more than once every three years. When discussing the CCC duration component, EPA (1985) states

> *An averaging period of four days seems appropriate for use with the CCC for two reasons. First, it is substantially shorter than the 20 to 30 days that is obviously unacceptable. Second, for some species it appears that the results of chronic tests are due to the existence of a sensitive life stage at some time during the test, rather than being caused by either long-term stress or long-term accumulation of the test material in the organism. The existence of a sensitive life stage is probably the cause of acute-chronic ratios that are not much greater than 1, and is also possible when the ratio is substantially greater than 1. In addition, some experimentally determined acute-chronic ratios are somewhat less than 1, possibly because prior exposure during the chronic test increased the resistance of the sensitive life stage. A four-day averaging period will probably prevent increased adverse effects on sensitive life stages by limiting the durations and magnitudes of exceedances of the CCC (page-5).*

However, EPA (2013, page 13) further specifies that a 30-day average may be utilized when exposure concentrations are shown to have "limited variability", as in the case of chronic exposure to ammonia. Therefore, for ammonia, both the 4-day average and a 30-day average will be assessed in conjunction for chronic exposure as cited in the Code of Maryland Regulations 26.08.02.03-2 (I):

> *(1) Averaging Period. The concentration of total ammonia nitrogen (in milligrams of nitrogen per liter) expressed as a 30-day average may not exceed the chronic criterion listed in Tables 1, 2 or 3….*
>
> *(4) In addition, the highest 4-day average within the 30-day period may not exceed 2.5 times the chronic criterion.*

In regards to the frequency component of aquatic life criteria, EPA (1985) states:

> *The abilities of ecosystems to recover differ greatly, and depend on the pollutant, the magnitude and duration of the exceedance, and the physical and biological features of the ecosystem. Documented studies of recoveries are few, but some systems recover from small stresses in six weeks whereas other systems take more than ten years to recover from severe stress. Although most exceedances are expected to be very small, larger exceedances will occur occasionally. Most aquatic ecosystems can probably recover from most exceedances in about three years.*

The nationally recommended criteria frequency and duration components are summarized in the following table. Maryland's assessment of water quality for the protection of aquatic life will incorporate these recommendations.

Criterion	**Duration**	**Frequency**
Acute	1-Hour Average	Not to be exceeded more than once every three years
Chronic	4-Day Average	
Chronic Ammonia	30-Day Average and 4-Day Average (2.5X)	

Assessment using Acute Aquatic Life Criteria

The duration component of acute aquatic life criteria is a one-hour average (EPA 1985). The ambient concentrations of water chemistry parameters are unlikely to vary significantly during a one-hour period. Furthermore, taking multiple samples during a one-hour period to estimate a one-hour average is often not practicable. Therefore, MDE will consider one water column sample showing a pollutant concentration above the magnitude component of the associated acute water quality criterion to be an exceedance. The aquatic life designated use is not supported if >1 of the samples exceeds the acute aquatic life criteria. As a general rule, Maryland will attempt to collect a minimum of 10 representative sampling events in a water body upon which to base an assessment. However, it should be noted that even with fewer than 10 samples, a water body will be listed as impaired on the Integrated Report if the acute aquatic life criterion is exceeded two or more times

Assessment using Chronic Aquatic Life Criteria

The nationally recommended duration component of chronic aquatic life criteria is a four-day average (EPA 1985). Unlike, the acute criteria, it is unlikely that a chronic exceedance can be identified using one sample because MDE cannot assume that one grab sample represents a four-day average. However, one or more grab samples showing a chronic exceedance may suggest that a chronic impairment is present. Therefore, MDE will perform additional statistical analysis on available data to estimate the likelihood of a chronic exceedance. The goal of this analysis will be to make statistical inferences about specific parameters (e.g. mean, median, other quantiles) against the applicable CCC. The choice of statistical test will depend on the several factors that include but are not limited to the following:

- Sample size
- Variance of the sample data
- Number of samples that exceed CCC
- Normality of the data
- Magnitude of exceedances
- Number of consecutive samples that exceed CCC
- Number of exceedances that occur within a certain time interval

If MDE determines that a chronic exceedance may have occurred, then the waterbody will be placed on Category 3 or Category 5, depending on the likelihood of impairment, and MDE will prioritize the water body for additional sampling efforts. The goal for such sampling efforts will consist of selecting 10 four-day periods over a 3-year time-span. For each four-day period, a minimum of 4 samples will be taken in order to calculate a four-day average. This will enable assessors to calculate 10 independent four-day averages. If >1 four-day period demonstrates an exceedance of the chronic criterion, then the waterbody will be placed on Category 5. The decision tree used for the assessment analysis is presented in Figure 1.

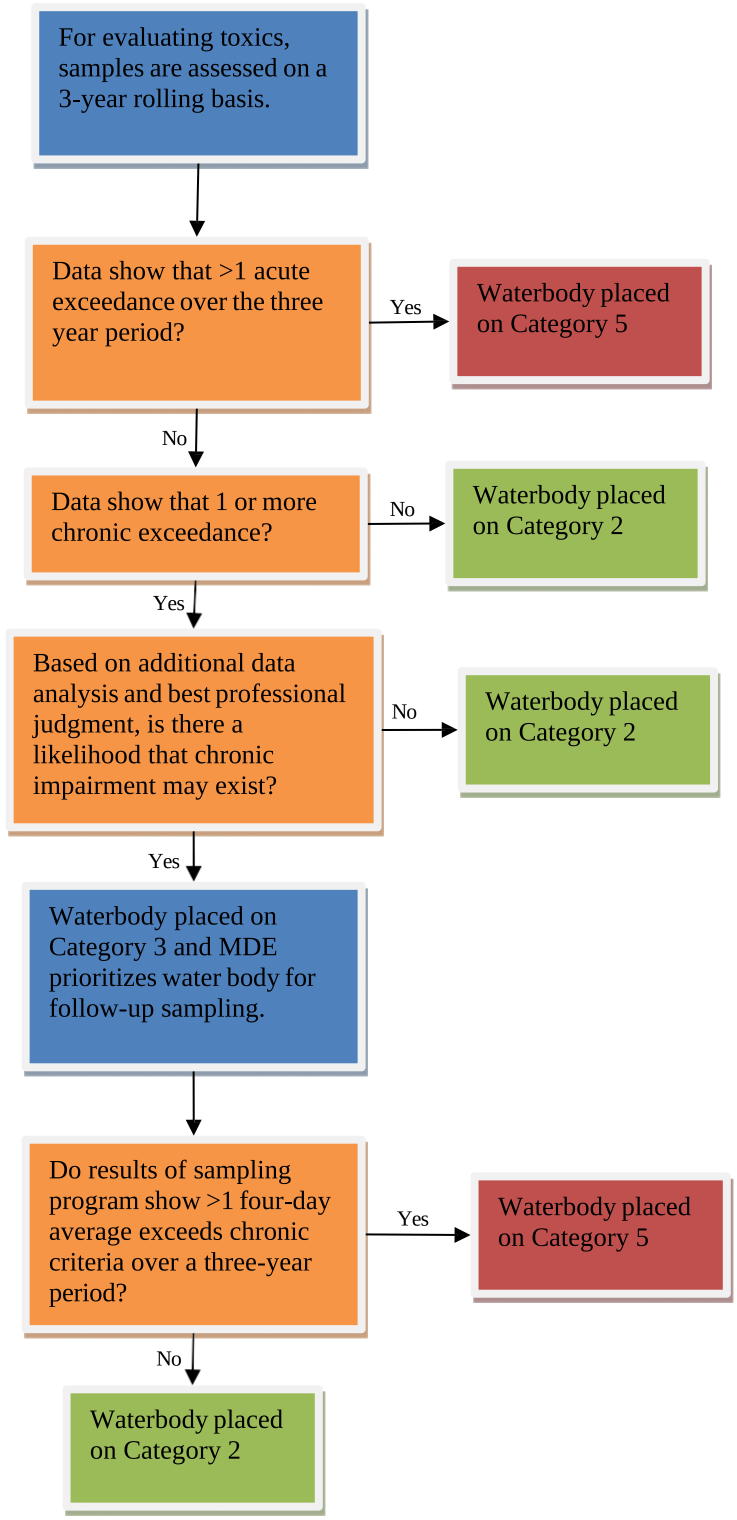

Figure 1. Chronic Aquatic Life Criteria Assessment Decision Tree

OTHER CONSIDERATIONS FOR WATER COLUMN ASSESSMENT

In addition to the ambient water quality data itself, Maryland will consider other factors such as:

- The magnitude of the criteria exceedance for any one contaminant.
- The number of criteria exceeded.
- Water column bioassay (toxicity) data indicating toxicity to test organisms.
- Data Quality.

If it is determined that a potential impairment exists [e.g. only one sample available (N=1) and it exceeds the acute criterion], but there is insufficient data to make an impairment determination, the segment will be placed in Category 3 (Insufficient data). The segment will then be prioritized for additional monitoring. In these instances, the Department will use its best professional judgment based on the available data to make its determination.

In the case that no criteria are available for a particular contaminant or no criteria are exceeded, other impairment indicators (e.g., ambient water column toxicity data) will be evaluated using best professional judgment. During this evaluation process, if toxicity is indicated, a Toxicity Identification Evaluation (TIE) may be considered to further identify the possible contaminant source(s) causing toxicity. A TIE is a comprehensive approach used in the Whole Effluent Toxicity (WET) Program to identify possible causes of toxicity. When warranted, MDE will also utilize spatial and temporal trend analyses as an additional evaluation tool for making impairment determinations.

As mentioned previously, MDE considers all existing and readily available data, including independent studies conducted by sources external to MDE. These ambient water column data are screened to determine if they are of acceptable quality (i.e., documented methods and an acceptable QA/QC plan). If the data are unacceptable (i.e., poor or no QA/QC) but suggest an exceedance of the appropriate criteria, the segment is targeted for additional monitoring, and evaluated using other approaches.

In many cases, there may be no ambient water quality data (chemical or toxicity) available for an impairment evaluation. In such cases, MDE will apply a weight-of-evidence approach using other data as described below.

SEDIMENT

Protecting sediment quality is an important part of restoring and maintaining the biological integrity of our State's waters. Sediment is an integral component of aquatic ecosystems, providing habitat, feeding, spawning, and rearing areas for many aquatic organisms. Sediment also serves as a reservoir for chemical contaminants and therefore a source of chemical contaminants to the water column and organisms. Chemicals that do not easily degrade can accumulate in sediments at much higher levels than those found in the water column.

Contaminated sediments can cause adverse effects in benthic or other sediment-associated organisms through exposure to pore water or direct ingestion of sediments or contaminated food. In addition, natural and human disturbances can release chemical contaminants to the overlying water, where water column organisms can be exposed. Sediment contaminants can reduce or eliminate species of recreational, commercial, or ecological importance, either through direct effects or by affecting the food supply that sustainable populations require. Furthermore, some chemical contaminants can bioaccumulate through the food chain and pose human health risks even when sediment-dwelling organisms are not themselves impacted. This specific pathway will be addressed later in the fish tissue approach.

MDE is using the following comprehensive weight-of-evidence approach in making impairment determinations. This approach, also referred to as the Sediment Quality Triad, consists of three components (Chapman 1992):

- Ambient Sediment bioassays - to measure toxicity
- *In situ* biological variables - to measure alteration of resident biota (*e.g.,* change in benthic community structure)
- Ambient Sediment chemistry - to measure chemical contamination

These components provide complementary data to each other, that when combined may provide an efficient tool in determining an impairment. However, each component has its limitations, which necessitates a sound scientific interpretation of the data and best professional judgment on a case-by-case basis. The scientific community, in fact, has previously indicated that sediment assessments are strongest when the three data components are used in combination to balance their relative strengths and weaknesses (Chapman 1992, Long et al. 2000, Anderson et al. 2001, Ingersoll et al. 1997, EPA 1997).

<u>Ambient Sediment Bioassay Data</u>

Ambient sediment bioassays are a type of biological data, in which test organisms are exposed under controlled conditions to the field collected sediment sample. Although we have confidence in this type of data because of the controlled conditions, it can be inconsistent, especially where toxicity is minimal or subtle. Laboratory artifacts, although generally controlled, can produce false results. For this reason, at least two or more nonmicrobial tests are required to exhibit toxicity to determine that the potential for adverse effects from contaminated sediment is high.

This type of data is essential in assessing sediment contaminants. If toxicity is exhibited to the tested benthic/epibenthic organisms, it is generally considered indicative of water quality that is incapable of supporting aquatic life, which is in violation of our State's water quality standards. Furthermore, it also suggests that the adverse effects observed in the toxicity tests may be related to chemical contaminants because other non-contaminant related causes (e.g. dissolved oxygen, pH, temperature) are controlled in the laboratory setting. In addition, the information from this data component is quantitative and can be correlated to the toxicity of other sediments or chemicals to the test species. For this reason, the greatest weight is given to toxicity test data among the three data components.

However, a limitation of this data is that it does not identify the causative pollutant, which necessitates the need for sediment chemistry data. The sediment chemistry data provides the best link for establishing an impairment determination resulting from contaminant exposure, which is the basis of this document. Additionally, the laboratory conditions under which bioassays are conducted may not accurately reflect field conditions of exposure to toxic chemicals, and thus introduces uncertainties when extrapolating to population dynamics. This point is important to understand because while attempting to control for non-contaminant related stressors (e.g., dissolved oxygen, pH, temperature), contaminants in the sediments may be rendered toxic to the test organisms that would not be toxic under field conditions, thus providing a false positive result (e.g., sulfide and ammonia in sediments, pH shift for metals). Additionally, a false-negative result could occur in sediment bioassays due to contaminants becoming non-bioavailable under test conditions (e.g., inorganic and organic metal complexes, pH shift lowering dissolved concentrations of metals).

Sediment Chemistry Data

Although EPA has been working on sediment quality criteria (SQC) for many years, no final numeric water quality criteria have been published. This is due to the difficulty in determining the fraction of the chemical contaminant that is biologically available to exert its toxic effect on the exposed population and in establishing a criteria derivation process that could be shown to be consistent with other evaluative tools. In fact, EPA has redirected their efforts to derive equilibrium sediment guidelines (ESGs), rather than criteria, for the following five substances; acenaphthene (EPA 1993a), fluoranthene (EPA 1993b), phenanthrene (EPA 1993c), dieldrin (EPA 1993d), and endrin (EPA 1993e).

In the absence of such guidelines, a set of screening values devised by National Oceanic and Atmospheric Administration (NOAA) has been generally accepted as a screening tool to evaluate the likelihood of adverse effects (Long and Morgan 1990; NOAA 1991; Long et al., 1995). The Effects Range-Median (ER-M) values are defined as the median (50th percentile) of the distributions of the effects data for a particular contaminant. However, these values should only be used to screen sediments for levels of possible concern, and should not be construed to indicate an adverse effect in the absence of additional corroborative data (Long and MacDonald 1998). In their development of a classification scheme for the National Sediment Quality Inventory, EPA also recognized the limitations of the ER-Ms by requiring that the bulk sediment chemistry data exceed two separate sediment benchmarks in classifying sediments as Tier I (probable adverse effects to aquatic life and human health) (EPA 1996).

In the absence of EPA ESGs and NOAA ER-M values, sediment quality benchmarks (SQBs) were derived by MDE for non-ionic organic substances using the EPA-recommended equilibrium partitioning approach, (e.g., alpha-BHC, beta-BHC, lindane, chlordane, chlorpyrifos, heptachlor, etc.) see Appendix A. This is also consistent with EPA's National Sediment Quality Inventory. MDE will compare sediment chemistry data according to the described thresholds in the following order:

a) EPA ESGs,
b) NOAA ER-M values,
c) MDE derived SQBs, and
d) Other toxicological sediment benchmarks (*i.e.,* toxicity data)

Both the quality of sediment chemistry data and associated screening thresholds are considered when conducting an evaluation. Once the quality of data has been established, the potential for adverse effect from contaminated sediment is said to be high if either of the following conditions are met:

1. The sediment chemistry data exceeded the EPA ESG, or

2. The sediment chemistry data exceeded the ER-Ms or other screening values by a factor of two[1] for any one contaminant, or

3. The mean ER-M quotient[2] is greater than 0.5 (Long et al. 2000; Anderson et al. 2001), or

4. The sediment chemistry data exceeded more than 5 ER-Ms[3] (Long et al. 2000; Anderson et al. 2001).

Furthermore, various environmental conditions in the sediment can have a profound effect on the availability and toxicity of the sediments to aquatic environment (e.g., AVS for metals, organic carbon for organics, etc.). If data on these parameters are available, MDE will use best professional judgment to interpret the effects of these parameters on the sediment chemistry data.

When the measured chemical exceeds the appropriate sediment threshold, any observed adverse effects to the test species may be due to the measured chemical with the likelihood increasing as the chemical concentration increases. When a chemical is

[1] The factor of two was derived as the geometric mean of the ratios for those substances for which ER-Ms and SQCs were available; acenaphthene (ER-M/SQC ratio=4.6), fluoranthene (ER-M/ESG ratio=0.6), and phenanthrene (ER-M/ESG ratio=1.6). Although it was possible to calculate a ratio for dieldrin (ER-M/ESG ratio=25), it was not considered because the ratio was greater than 5 times the highest of the other three ratios. This condition serves the purpose of confirming the severity of contamination for any one contaminant above background concentrations, and therefore demonstrating the potential for impairing that segment.
[2] An ER-M quotient is calculated as the ambient sample concentration over the ER-M (toxicity weighted average).
[3] Long et al., (2000) showed that there is a much higher probability (>48%) that samples would be toxic in which six or more ERM values are exceeded or in which mean ERM quotients exceed 0.5.

measured at a level below the threshold, any observed adverse effects are not likely to be due to the measured chemical. It is recognized, however, that sediments are rarely, if ever contaminated by a single chemical. Therefore, in cases where a chemical is measured at a level below a threshold, the sediment may still cause adverse effects. Such cases could include, for example, contaminated sediments where chemicals not covered by a threshold are creating or contributing to toxicity, or where bioaccumulation or biomagnification up the food chain is a concern (EPA 2000).

The mere exceedance(s) of a sediment threshold, however, does not in itself establish an adverse effect from toxicity, but helps to identify the chemical that might be responsible for any observed adverse effects from toxicity. Given these limitations, MDE does not believe that the exceedance(s) of sediment thresholds are appropriate as sole indicators of use attainment. Instead, we recommend using all three data components as a basis for interpreting narrative criteria and developing pollutant reduction strategies.

Biological Benthic Assessment Data

In freshwater, MDE currently uses biological community data independently in making an impairment determination. The methodology dealing with biological assessments is addressed elsewhere under the biocriteria framework. This type of data is generally considered a good water quality indicator, because it measures a community (population) response to water quality and integrates through time and cumulative impacts. To determine toxicity for parameters without a water or sediment quality criterion, if these assessment data or other types of assessment data (e.g. Chesapeake Bay restoration goals) do not indicate an alteration (or degradation) of the biological benthic community, the water body may not be considered for an impairment determination despite data from the other components because:

1. It is supportive of aquatic life (at a community level), and thus meets its designated use,

2. The biological assessment component is a more rigorous method of assessing water quality than chemical and bioassay data which may be highly dependent on uncontrollable variables

3. It measures a community response to water quality rather than subjective endpoints from the other components (*e.g.* ER-M, significant level of toxicity, toxicity to one species)

4. It is consistent with the biological assessments method developed elsewhere

It is more likely to observe an alteration of the biological community where none should be present (false positive) than not to observe alteration of the biological community where one should present (false negative). Anderson et al., 2001 found that laboratory toxicity tests were indicative of benthic impacts in Los Angeles and Long Beach Harbor stations in California. Single and multivariate correlations showed significant positive relationships between amphipod survival in laboratory toxicity tests and measured benthic community structure in field samples. For this reason, MDE would further investigate the chemistry and toxicity data where an alteration of the biological community has been observed. These data would be used to confirm that the community effect is due to exposure to contaminants and to identify the probable contaminant of concern. However, although biological assessment data alone could indicate an impairment, it would not necessarily result in a "toxics" impairment determination. This is because non-contaminant effects (e.g., competition, predation, sediment type, salinity, temperature, recent dredging) may confound interpretation of this data with respect to chemical contamination by toxics (Anderson et al. 2001).

Weight-of-Evidence Approach (Sediment Quality Triad)

A comprehensive approach using multiple assessment methods helps eliminate false conclusions brought about by relying solely on one method of evaluation. Consequently, MDE would assess sediment quality, and thus an impairment determination, using a weight-of-evidence approach (Winger et al. 2001). Biological assessments could be used to supplement findings of impaired waters, or as a prioritization tool to determine where additional testing should be performed. These components provide complementary data to each other, which when combined may provide an efficient tool in determining an impairment. However, each component has its limitations, which necessitates a sound scientific interpretation of the data and best professional judgment on a case-by-case basis. Consequently, the individual use of these data components as sole indicators of use attainment is inappropriate. Instead, we recommend using all three data components as a basis for interpreting narrative criteria and developing pollutant reduction strategies.

Sediment chemistry data provide information on contamination, and when used with sediment thresholds or other indicators, also provide insight into potential biological effects. However, they provide little insight on the bioavailability of the contaminant unless data on other mitigating factors (e.g. AVS for metals, organic carbon for organic contaminants) are collected simultaneously. Sediment bioassays are an important component of sediment assessment because they provide direct evidence of sediment toxicity. However, they do not identify the causative pollutant. Additionally, the laboratory conditions under which bioassays are conducted may not accurately reflect field conditions of exposure to toxic chemicals. In situ biological studies (such as benthic community composition analyses) are useful because they account for field conditions. However, interpretation with respect to chemical contamination may be confounded by non-contaminant effects. Because each component alone has limitations, the Triad approach uses all three sets of measurements to assess sediment contamination. Table 1 lists possible conclusions that can be drawn from various sets of test results, followed by possible listing decisions.

Table 1: Possible Conclusions Provided by Using the Sediment Quality Triad Approach (Chapman 1992).

Scenario	Toxicity	Chemistry	Community Alteration	Possible Conclusions	Listing Decision
1	+	+	+	Strong evidence for chemical contaminant-induced degradation.	List (Part 5)
2	-	-	-	Strong evidence for absence of chemical contaminant-induced degradation.	Do not list for toxics
3	-	+	-	Chemical contaminants are not bioavailable.	Do not list for toxics
4	+	-	-	Unmeasured chemical contaminants or conditions may exist that have the potential to cause degradation.	Do not list for toxics Additional monitoring
5	-	-	+	Alteration is probably not due to chemical contaminants.	Do not list for toxics
6	+	+	-	Chemical contaminants are likely stressing the system.	List (Part 3) Additional monitoring
7	+	-	+	Unmeasured chemical contaminants are causing degradation.	List (Part 3) Additional monitoring
8	-	+	+	Chemical contaminants are not bioavailable or alteration is not due to contaminants.	Do not list for toxics Additional monitoring

"+" Indicates measured difference between test and control or reference conditions.
"–" Indicates no measurable difference between test and control or reference conditions.

As indicated in Table 1, there may be scenarios where sediment chemistry data, sediment bioassays, and benthic community analyses produce conflicting results. In these scenarios, the interpretation becomes more complex, but it does not necessarily indicate that any of the data sets are "wrong", although this possibility should not be ruled out without sound evidence.

Scenario #1: This decision is due to the overwhelming evidence of impairment from all three data components.

Scenario #2: This decision is based on the overwhelming lack of evidence from all three data components.

Scenario #3: Without evidence of toxicity or a degraded biological community, the most likely conclusion is that the chemical contaminants, although elevated, are not bioavailable. If the biological community data shows no adverse effect, the water quality is deemed to be supportive of aquatic life and its designated use is fully supported.

Scenario #4: The basis for this decision is due to the biological community response, and is supported by sediment chemistry. The clear results from the healthy biological community and the lack of chemical concentrations consistent with toxic impacts suggest that the toxicity test results may be anomalous, due to artifacts and not to chemical contaminants. It is possible that there are unmeasured contaminants, but the impact is not sufficient to impair the designated use, as demonstrated by the biological community. However, if the magnitude of the effect observed in the bioassays were severe (e.g. <50 percent survival), the Department may re-evaluate its listing decision. Nevertheless, additional monitoring would be required to confirm the findings of the Triad, and to determine if further actions are required.

Scenario #5: Without evidence of toxicity or elevated chemical concentrations, the most likely conclusion is that the degraded biological community is not due to chemical contaminants. This scenario, however, will be captured by other decision rules.

Scenario #6: Where a good tool exists for evaluating the biological community, it is usually a good indicator of water quality in general and is very sensitive because it integrates impacts from different stressors as well as impacts through time. Practical experience has shown that where "IBI"-type indicators are considered, they indicated impairments not supported by the other data components (i.e., toxicity and chemistry). Therefore, where biological community data of this type exist showing non-degraded biological communities, it will be considered as sufficient evidence of a supported designated use, despite the implications of toxicity and chemistry.

However, where no such data exists or where those indicators are not applicable, the Department will apply its best professional judgment, but will likely determine that the designated use is not supported.

Scenario #7: The basis for this decision is the adverse response observed from the toxicity and biological community data. In this scenario, the water quality is not supportive of aquatic life and is likely due to a chemical contaminant(s) with no applicable chemical threshold or some unmeasured chemical contaminant. This scenario would require listing in Category 3 of the Integrated Report. Additional monitoring would be required to determine the impairing substance(s).

Scenario #8: The basis of this decision is the absence of effect in the bioassays. Although the biological community show adverse effects, the lack of toxicity in the tests are indicative that the adverse effect is not due to chemical contaminants, or that they are not bioavailable. If chemical contaminants were truly affecting the designated use, the impacts of those contaminants should have been observed in the bioassay. These bioassays control for confounding factors such as low dissolved oxygen, or habitat impacts. This scenario, however, will be captured by other decision rules.

The scientific community has indicated that in order to obtain a reliable and consistent assessment, data from all three components (i.e., toxicity, chemistry, and biological community) are required (Chapman 1992, Ingersoll et al. 1997, Long et al. 1998, Long et al. 2000 and Anderson et al. 2001). However, if data are not available for all three components, the Department will use its discretion but will consider an impairment determination if;

a) If the magnitude of any single indicator is overwhelmingly suggesting an impairment determination,
b) If a toxicity test shows toxicity and is confirmed either by chemistry data or a degraded biological community, its designated use is not likely supported and an impairment determination will likely be concluded.
c) All other cases are considered to present insufficient evidence of impairment and will be prioritized for additional monitoring as resources become available.

Under the Triad approach, MDE would evaluate appropriate lethal and sublethal sediment bioassays. A finding of toxicity may trigger a sediment chemistry analysis, if one has not already been performed. Sediment chemistry data would be used to support an impairment determination. The chemical analysis should be performed on samples originating from the same composited homogenate used for the bioassays, so that paired data can be obtained (Chapman 1992). The chemistry data can be compared to sediment thresholds to help determine which chemicals may be causing toxicity. If no sediment thresholds are exceeded, sediment Toxicity Identification Evaluation (TIE) should be performed to determine a chemical cause if possible.

Chemistry data themselves are useful in determining sediment contamination trends, and may also help identify areas that may have the potential for adverse impacts. MDE uses sediment chemistry data, as an effective prioritization tool to help determine which sediments should be targeted for additional monitoring. That is, other factors being equal, sediments with chemical concentrations exceeding sediment thresholds would have higher priority for further testing compared with sediments that meet the sediment thresholds. Chemical concentrations exceeding these thresholds could also indicate the need to monitor and assess water column concentrations for those chemicals. Sediment chemistry alone should not, however, be used to make an impairment determination.

FISH TISSUE

Section 101(a)(2) of the Clean Water Act established as a national goal the attainment of "water quality which provides for the protection and propagation of fish, shellfish, and wildlife, and recreation in and on the water." This is commonly referred to as the "fishable/swimmable" goal of the Act. Additionally, Section 303(c)(2)(A) requires water quality standards to protect the public health and welfare, enhance the quality of water, and serve the purposes of the Act. The Environmental Protection Agency (EPA), along with Maryland Department of the Environment (MDE), interprets these regulations to mean that not only should waters of the State support thriving and diverse fish and shellfish populations, but they should also support fish and shellfish which, when caught, are safe to consume by humans.

Maryland monitors across the state to identify potential fish consumption hazards. The fish targeted for collection include popular recreational fish species (e.g., striped bass, catfish, etc.). Eels, fallfish, and other species are collected when target species are not readily available (MDE 2019). Monitoring has revealed contaminant levels in certain areas. MDE routinely monitors watersheds within five zones: freshwater in Western Maryland, non-tidal waters in the Baltimore/Washington metro area, tidal waters in harbors and bays, tidal waters in Western bay tributaries, and tidal and non-tidal waters on the Eastern Shore. Monitoring of these affected areas are conducted to verify and identify appropriate species and size classes associated with harmful contaminant levels. Findings from such studies are the basis for fish consumption guidelines and Integrated Report assessments.

For each waterbody of interest, there may be chemical-specific data from several resident fish that are used in the tissue analysis for fish consumption advisories and Integrated Report Listings. Some contaminants found in Maryland waters (e.g., mercury and PCBs) tend to bioaccumulate to elevated levels in the tissues of gamefish (e.g. largemouth bass) and bottom-feeders (e.g. catfish). The tissues of interest include the edible portions of fish (i.e., fillet), crab (crabmeat and "mustard"), and shellfish ("meats"). MDE personnel are responsible for the collection and in-field processing of fish samples. Sampling teams determine the method used to fillet each fish (e.g., with or without skin and/or ribs, no dark meat or belly fat) which is dependent on the species of fish (EPA 2000a, MDE 2018). MDE has Standard Operating Procedures for the methods used in preparing fish samples, and has ensured that the sample used for assessing a water body is consistent with water quality criteria (MDE 2018; EPA 2010). All of the fish species collected by MDE sampling teams are deemed to be representative of the existing fish populations in a waterbody.

Fish tissue from the edible portion of five or more fish may be processed individually, i.e., discrete sample analysis, or all together as a single composite sample[4]. All of the fish

[4] Fish tissue is usually analyzed as a multiple fish composite sample. Sometimes for mercury samples, individual fish are analyzed separately while for PCBs, usually all of the fish are combined into a composite before analyzing.

that comprise a sample must be within seventy-five percent of the total length of the largest fish. Either one of these analytical methods can be used for an assessment:

- For composite sample analysis, five or more fish fillets are ground and blended together to create a single composite sample for contaminant content analysis.
- For discrete sample analysis, five or more individual fish fillets are ground and blended separately. Each of the blended samples are analyzed for contaminant content and the median result is used in the assessment process.

An estimate of central tendency, i.e., the median value, is used in the analysis of fish data. The median value represents the measured concentration of the contaminant in the edible portion of the fish tissue. Further information regarding analysis methods can be found in the technical support document provided at MDE's fish consumption advisory webpage (MDE 2019).

Fish Tissue Data Use for Fish Consumption Recommendations and Advisories

When tissue levels of a specific contaminant are elevated to increase the risk of chronic human health effects, the State has the responsibility to issue a fish consumption advisory (MDE 2019, EPA 2000b). The minimum data requirements for a fish consumption advisory sample is 5 resident fish of the same species. A single exceedance of contaminant limits by one sample (i.e., a composite sample of 5 fish) is sufficient to issue a fish consumption advisory. Once a fish consumption advisory is issued for a waterbody and fish species, that advisory will remain in effect until future sampling efforts provide comparable data that does not exceed threshold/criterion limits.

In general, fish tissue concentration data for a specific waterbody will be drawn from the most recent year of fish sampling. However, in some cases, additional data from sampling up to 4 years prior may be included in the determination of the median value for the waterbody for a fish consumption advisory (MDE 2019). Fish consumption advisories are designed to protect the general as well as sensitive populations (i.e., young children; women who are or may become pregnant). MDE provides specific meal recommendations of up to 8 meals per month after which there is no limit. Fish consumption advisories are typically issued in those situations where consuming 8 or fewer meals of fish per month (96 meals per year) from the waterbody is associated with a lifetime cancer risk greater than 10^{-5} (i.e., 1 additional possible cancer case in a population of 100,000 people) (MDE 2019).

Fish Tissue Data Use for Integrated Report Listings

It has been accepted that when a fish consumption advisory is issued for a waterbody, the designated use of that waterbody is not being supported. If the minimum data requirement is met, this usually results in listing a waterbody as impaired for the specific contaminant. Data requirements for Integrated Report assessments differ from those used for fish consumption advisories.

The data requirements for listing a waterbody as impaired are as follows:

1. Minimum data requirement: 5 fish of the same resident species for a given waterbody. Fish tissue may be analyzed as discrete samples in which a median result is produced, or as a single composite. Either analysis method may be used.
2. All of the fish that comprise a composite, or individually analyzed samples, must be within the same size class, i.e., the smallest fish must be within seventy-five percent of the total length of the largest fish.
3. The size of the fish sampled must be the legal size for possession within Maryland (MDNR 2019). If no minimum size limit exists for a specific species, best professional judgment for a minimum size of a given species will be applied.
4. Only samples taken from the part of the fish, crab, or shellfish typically consumed will be used for human health assessment purposes, i.e., assessing the attainment of the fish consumption use. In Maryland, the publication of advisories for fish is based solely on contaminant concentrations found in fillets. Therefore, only data on fillets are to be considered for making impairment decisions. For shellfish (i.e., oysters and clams), only the soft tissue portion will be considered. Studies show that both crab meat and the crab hepatopancreas (i.e. mustard) are frequently consumed, therefore, individual consumption advisories are published for both portions. However, because crabs are migratory, they are not typically used, on their own, to determine a fish consumption impairment.
5. Species used to determine impairment should be representative of the waterbody. Migratory and transient species may be used if they are the dominant recreational species, but should only be used in conjunction with resident species, especially in the case of tidal tributaries of the Chesapeake Bay.

All available data within a ten-year period are compiled and assessed when making impairment decisions. MDE calculates the median value for all data collected on a single fish species over the ten-year period. A median value of the contaminant level in the edible portion of a common recreational fish species is then compared to the established threshold/criterion.[5] If any single fish species median value exceeds the threshold/criterion, that waterbody's designated use is not met, and the waterbody is listed as impaired. The Department reserves the right to use best professional judgment when reviewing data collected over the 10-year period that may have major comparability concerns (e.g. different species collected). However, in general, MDE assessors will operate under the assumption that sample collections are representative of the predominant recreational fish community at the time they are collected (both in terms of species and size). If samplers are no longer able to collect a species that was previously collected and found to have high levels of a contaminant, assessors will take under consideration the attempts made to collect this species and whether it is still representative of the common recreational fish species found at the water body. In some cases, such a fish species may not exist in great enough abundance to serve as a useful

[5] Note: This median is calculated either from the analysis of individually tested fish or from the results of multiple fish composites (e.g. 2 composites of 5 fish each) depending on how the fish tissue samples were analyzed. Sometimes for mercury samples, individual fish in a composite are analyzed separately while for PCBs, usually all of the fish in a composite are combined before analyzing.

measure of fish consumption risk for Integrated Report assessments and so assessors may use other species to determine the updated impairment status.

To ensure that an impairment is temporally relevant, impairments based on the minimum required samples should be re-sampled prior to TMDL development. Follow-up monitoring is also conducted periodically to assess changes in the contaminant levels in selected fish species.

Contaminant Thresholds

The existing fish tissue criteria are used as the listing thresholds (e.g. methylmercury fish tissue criterion: 300 ppb). For contaminants that do not have an existing criterion (e.g. PCBs), MDE has defined "fishable" as the ability to consume AT LEAST 4 meals per month of common recreational fish species by a 76 kg individual. In such cases, the fish tissue concentration threshold used for impairment listing is the concentration that results in a 4 meals per month advisory (see Contaminant Thresholds Section). The acceptable contaminant thresholds are based on a risk assessment calculation that incorporates numerous risk parameters such as contaminant concentration, reference dose/cancer slope factor, exposure duration, lifetime span, and for some contaminants, cooking loss.

Table 2: Concentration thresholds/criterion for the contaminants of concern.

Contaminant	Threshold/Criterion	Basis	Group
Chlordane	242.8 ppb (ng/g – wet weight)	4 meals/month concentration level	76 kg Individual
Heptachlor Epoxide	9.3 ppb (ng/g – wet weight)	4 meals/month concentration level	76 kg Individual
Mercury[6]	300 ppb (ng/g – wet weight)	EPA/MDE Fish Tissue Human Health Consumption Criteria	76 kg Individual
PCBs (Polychlorinated biphenyls)	39.0 ppb (ng/g – wet weight)	4 meals/month concentration level	76 kg Individual
PFOS (Perfluorooctane sulfonic acid)	5.1 ppb (ng/g- wet weight)	4 meals/month concentration level	76 kg Individual

Over time, advances in science may require changes in risk assessment parameters that may increase or decrease the currently used contaminant thresholds, and consequently the levels at which impairment decisions are made. When this happens, waters may need to be re-assessed.

[6] Per EPA recommendation, total mercury concentrations, as opposed to methylmercury, will be used in MDE fish consumption risk-calculation. This approach is deemed to be most protective of human health and most cost-effective.

GEOGRAPHIC SCALE OF ASSESSMENT

Starting with the 2012 Integrated Report, all water quality assessments have been georeferenced according to the real-world waters that they represent. In order to maintain consistency with respect to assessment scale, MDE has adopted the following protocols for specific toxics assessments.

Water Column and Sediment

Toxics data collected as part of a water column or sediment study will be assessed on a reasonable and flexible scale. In some cases, only a single location may have been sampled, while in others, samples may have been collected in transect. In either case, MDE will exercise best professional judgment in applying assessment results to a particular geographic area. Unique geographic and/or data scenarios require maximum flexibility to ensure that assessments are representative of a particular water body. For this reason, MDE will adapt its water column and sediment toxics assessment scale to circumstances as necessary.

Fish Tissue

Fish tissue data are typically collected from the following three water body types: 4^{th} order or greater non-tidal rivers, impoundments, and estuarine segments. Since fish are mobile, MDE uses this data to assess appropriately sized expanses of water. For non-tidal rivers, MDE assigns the assessment result from a composite to the entire mainstem of the sampled stream up to the headwaters. Side tributaries to the mainstem are not included in the assessment as they do not always support gamefish in sufficient numbers or size to enable sampling. For impoundments, assessment results will only be applied to the polygonal area of the impoundment's surface. Fish tissue results will not be applied to any part of the upstream watershed. Lastly, fish tissue data collected from estuarine waters will be used to assess only the tidal waters of the 8-digit watershed from which the fish were collected. Again, the assessment for a tidal water body will not be applied to any upstream waters, regardless of whether the upstream waters are tidal or non-tidal.

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Appendix A: Table of Sediment Screening Values.

Contaminant	Sediment Screening Values (ppb)		
	EPA SQCs	NOAA ERMs	MDE SQBs
α-BHC			4,357
Acenaphthylene		640	
Acenaphthene	2,300	500	
Anthracene		1,100	
Arsenic		70,000	
β-BHC			9,406
Benz(a)anthracene		1,600	
Benzo(a)pyrene		1,600	
Cadmium		9,600	
Chlordane		6	51
Chlorpyrifos			4,214
Chromium		370,000	
Chrysene		2,800	
Copper		270,000	
DDT Sum		46	
Dibenz(a,h)anthracene		260	
Dieldrin	200	8	3,616
Endrin	7.6		7,368
Fluoranthene	3,000	5,100	
Fluorene		540	
Heptachlor			1,433
Heptachlor epoxide			1,433
Hexachlorobenzene			6,114,892
Lead		218,000	
Mercury		710	
Methyl naphthalene, 2-		670	
Naphthalene		2,100	
Nickel		51,600	
p,p-DDD (TDE)		20	
p,p-DDE		27	
p,p-DDT		7	
PAHs (High MW)		9,600	
PAHs (Low MW)		3,160	
PAHs (Total)		44,792	
PCB (Polychlorinated Biphenyl)		180	
Phenanthrene	2,400	1,500	
Pyrene		2,600	
Silver		3,700	
Zinc		410,000	