

# **Evaluation of Water Quality Translators for Mercury**

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## ABSTRACT

This report discusses the technical issues and constraints associated with translation of a mercury fish tissue concentration into a water quality criterion, in the use and implementation of the Environmental Protection Agency's fish-tissue-based criterion for methylmercury (0.3 mg methylmercury/Kg wet weight fish tissue). The report focuses on available analytical methods for evaluating mercury in fish and water; proposed methods for translating a fish tissue concentration for mercury into a concentration in water; and implementation of the mercury criterion in the development of Total Maximum Daily Loads (TMDLs) and water quality-based effluent limits (WQBELs). The approaches to criteria translation are, in order of preference: (1) derive site-specific bioaccumulation factors (BAFs), (2) use a bioaccumulation model, or (3) use EPA's national default translators. The collection of site-specific data allows for the most accurate assessment of bioaccumulation; however, validation of methylmercury analytical techniques is necessary to increase the certainty of results. Models have the potential to account for environmental factors contributing to data variability, but at present the available models are limited to reservoirs and lakes in a few geographic regions. Improvements in national default translators do not decrease the importance of site-specific translators. National default values are likely to be inaccurate on a site-specific basis, given the very high degree of variability observed in mercury bioaccumulation rates. Research is needed to improve the national default translators currently proposed by EPA, and additional data would increase the effectiveness of the translator calculation methods by reducing variability and minimizing the uncertainty of the resulting default values. Given the many uncertainties associated with mercury translators, their use should be limited to cases where site-specific fish tissue data reveal the tissue-based water quality criterion has been exceeded, and point sources make up a significant contribution of the total mercury loading to the water body.



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## LEGEND

AVS	acid volatile sulfide
BAF	bioaccumulation factor
CMC	Criteria Maximum Concentration
CWA	Clean Water Act
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
ELG	effluent limitation guideline
FAV	Final Acute Value
FCV	Final Chronic Value
$f_d$	dissolved methylmercury as fraction of total mercury in water column
$K_D$	partition coefficient, dissolved methylmercury to particulate mercury
MS/MSD	matrix spikes and matrix spike duplicates
NAWQA	national ambient water quality assessment
NPDES	national pollutant discharge elimination system
NIST	National Institute of Standards and Technology
OPR	ongoing precision and recovery
PAH	polycyclic aromatic hydrocarbon
PBT	persistent bioaccumulative toxic
POTW	publicly owned treatment works
QA	quality assurance
QC	quality control
RPA	reasonable potential analysis
SOP	standard operating procedure
TMDL	total maximum daily load
TSS	total suspended solids
WLA	wasteload allocation
WQBEL	water quality based effluent limit
WQS	water quality standard



# Evaluation of Water Quality Translators for Mercury

## Executive Summary

This report was prepared for the purpose of presenting an overview and discussion of the use of the ambient water quality criterion for methylmercury developed by the U.S. Environmental Protection Agency (EPA) in 2001 (66 FR 1344). Unlike all other previous water quality criteria for the protection of human health, the criterion for methylmercury was issued as a fish tissue concentration (i.e., 0.3 mg methylmercury/Kg wet weight fish tissue), because the fish consumption pathway is the main route of exposure to mercury in the environment. As a result, enforcement of water quality standards based upon this criterion requires either fish tissue sampling or the conversion of the criterion to a concentration in water, especially for the development of National Pollutant Discharge Elimination System (NPDES) permits.

Because many permitted dischargers will be faced with meeting the methylmercury criterion, this report focuses on (1) available analytical methods for evaluating mercury in fish and water; (2) proposed methods for translating a fish tissue concentration for mercury into a concentration in water; and (3) implementation of the mercury criterion in the development of Total Maximum Daily Loads (TMDLs) and water quality-based effluent limits (WQBELs). EPA (2002a, 2004a) draft *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* addresses these issues and is discussed where applicable.

## Analytical Methods

Analytical methods to quantify mercury in environmental samples continue to be refined. EPA Method 1631 is currently used to measure total mercury in water samples, while EPA Method 747B/SW-846 can be used to analyze total mercury in solid or semi-solid samples. The basic method for quantifying methylmercury is EPA Method 1630. Modifications to this method are described in the UW-Madison Standard Operating Procedure (SOP) and the United States Geological Service (USGS) Method. The selection of a method to test for either total mercury or methylmercury should be based on several factors, including method detection limit, validity of the method, and quality control procedures. All of these factors are important because they determine the quality and usability of the generated data.

## Mercury Translation

The translation from methylmercury in fish to total mercury in water can be viewed as a single step (i.e., the direct method) or a multi-step process. In the direct method, total mercury in fish is directly translated to total mercury in water. In contrast, in the multi-step approach methylmercury in fish is converted to dissolved methylmercury in water and then to total mercury in water. The major challenge in developing mercury translators is the enormous variability in the site-specific potential for mercury methylation and bioaccumulation. Among the important factors that contribute to the variability in mercury bioavailability and bioaccumulation are pH, dissolved organic carbon (DOC), salinity, water flow (e.g., stream flow, lake flushing rate, etc.), temperature, reduction-oxidation potential, sulfide and sulfate, suspended solids, nutrient loading, fish age and size, prevalence of wetlands and forested land cover in the watershed, and concentration-dependent demethylation (Brumbaugh et al. 2001; Qian et al. 2001; Kamman et al. 2004; Marvin-DiPasquale et al. 2000; Sonesten 2003a; Rose et al. 1999; Ullrich et al. 2001; Watras et al. 1998).

EPA (2002a, 2004a) draft guidance recommends the following approaches to criteria translation, in order of preference: (1) derive site-specific bioaccumulation factors (BAFs), (2) use a bioaccumulation model, or (3) use EPA's national default translators (EPA 2004a). EPA (2004a) does not recommend any specific bioaccumulation models for mercury, although a modeling approach is preferred over the use of default translators. Despite extensive study, there are no accurate, nationally applicable models for predicting mercury bioaccumulation. As an alternative to process-based or mechanistic mathematical models, the draft EPA guidance suggests that regression models incorporating such variables as pH, DOC, and fish age may be acceptable for criteria translation purposes.

In addition, the draft EPA guidance includes empirically-derived default values to simplify the translation from the fish tissue criterion to a water quality criterion for total mercury. Two sets of values are provided: (1) BAFs describing the relationship between dissolved methylmercury in water and methylmercury in fish, and (2) fraction dissolved ( $f_d$ ) values describing the relationship between total mercury and dissolved methylmercury in water.



Moreover, the guidance describes partition coefficients ( $K_D$  values) that account for the role of total suspended solids (TSS) in determining dissolved mercury concentrations, although default values are not identified.

Despite the identification of default translators, the preferred approach to criteria translation, as recommended by EPA, is the use of site-specific translators. Provided that the study design accommodates an expectation of high variability, it should be possible to effectively develop site-specific translators for mercury.

### **Mercury Translations in TMDL/Permits**

For many facilities, the major issue in developing mercury translators is incorporating the fish tissue mercury criterion into a discharge permit limit. Permits may be reopened and reassessed as part of a TMDL implementation. At least 45 states have fish consumption advisories due to mercury and over 1,000 water bodies are listed as being impaired due to mercury, thus triggering TMDLs. Several methods are generally used in developing mercury TMDLs: (1) the concentration in fish tissue; (2) the concentration in the water column; or (3) the concentration in sediment. Of the three methods, using a fish tissue concentration as the TMDL target is the most direct measure of the desired endpoint, protection of human health.

Determining how to allocate loadings among point and nonpoint sources is the next major part of a TMDL. EPA (2002a, 2004a) offers three approaches to allocation of loadings, depending upon the relative contributions of point source and nonpoint source loadings. First, where point source loadings dominate, the TMDL should specify reductions in these loadings, alone or together with nonpoint source loadings, to attain water quality standards (WQS). Second, where point source loadings are small, reductions in nonpoint sources are expected to achieve the TMDL. The third scenario also involves relatively small contributions from point sources, but reductions in nonpoint sources are not expected to be sufficient to attain WQS.

The approaches used to implement a mercury TMDL will vary depending upon the allocations, as described above. Where there are waste load allocations (WLAs) to point sources, the traditional method to implement a TMDL is likely to be used (i.e., through the NPDES permit). The implementation of effluent limitations for mercury and other pollutant parameters can be approached through several mechanisms including reasonable potential and development of WQBELs. Where a permittee anticipates mercury limits being incorporated into their permit, they should be prepared to proactively take steps to understand the concentrations of mercury that are discharged from their facility (and the nature of these sources), the receiving stream characteristics (including sediment and aquatic species), and the policies of permitting and regulating mercury by the permitting authority. Despite the cost, collection of site-specific data affords dischargers opportunities to develop more realistic bioaccumulation scenarios, potentially allowing the calculation of a more appropriate water quality criterion.

### **Summary and Recommendations**

This report summarizes the issues associated with translation of a mercury fish tissue concentration into a water quality criterion. Section 2 presents an overview of the analytical methods available for analyzing total mercury and methylmercury in fish tissue, water, and sediment. Section 3 provides an analysis of the methods and models available to translate the fish tissue concentration into a water quality criterion. Section 4 describes the impacts of the mercury water quality criteria on TMDL development and NPDES permits. Finally, Section 5 discusses the applicability of these issues for other metals. Although the report addresses many topics, it also identified several areas where additional research or study is necessary to fully understand mercury translation in the environment. The following bullets summarize the key findings and recommendations for additional study:

- Validation of methylmercury analytical techniques is necessary to increase the certainty of results.
- Research is needed to improve the national default translators currently proposed by EPA. EPA's data set of BAF,  $f_d$ , and  $K_D$  values should be updated with more recent studies. Additional data would increase the effectiveness of the translator calculation methods by reducing variability and minimizing the uncertainty of the resulting default values.
- National default values are likely to be inaccurate on a site-specific basis, given the very high degree of variability observed in mercury bioaccumulation rates. Models have the potential to account for environmental factors contributing to this variability, but at present the available models are limited to reservoirs and lakes in a few geographic regions.
- Improvements in national default translators do not decrease the importance of site-specific translators. It is feasible to develop site-specific translators, although the level of sophistication will be driven by costs



associated with data collection and testing. As the complexity of the site increases, the perceived need to investigate factors that may contribute to spatial or temporal variation in mercury bioaccumulation will also increase.

- Given the many uncertainties associated with mercury translators, their use should be limited to cases where fish tissue data show exceedance of the tissue-based water quality criterion, and point sources make up a significant contribution to mercury loading in the system. This recommendation is in contrast to the draft EPA guidance, which would allow states to adopt water-based rather than tissue-based mercury criteria for the protection of human health.
- Underlying the use of any type of mercury translator is the premise that mercury levels in fish will respond in a linear manner to reductions in mercury loading.
- It is reasonable to assume that the states, given their lack of resources, will follow the simplest approach, whether or not it is the most scientifically valid. Thus, whole waterbodies or even entire states are likely to be designated impaired and subject to TMDL analyses due to levels of methylmercury in fish, regardless of whether or not site-specific data exist.
- Changes to permit limits are likely to be derived in the absence of a RPA and the accurate consideration of non-point source contributions. To allow permit revisions, many states may default to a state-wide BAFs to allow translation of the fish tissue criterion into a water column value, which can then be implemented in NPDES permits in the traditional manner.
- As the use of EPA Method 1631 becomes more widespread, many dischargers are expected to face extremely low permit limits. At a minimum this will likely entail monitoring for mercury and developing a plan to minimize mercury in discharge waters. In some cases, permittees may be required to monitor ambient waters and local fish tissue.
- The collection of site-specific data affords dischargers opportunities to develop more realistic bioaccumulation scenarios. The cost of this could be shared between groups of dischargers within a waterbody.

## 1 Introduction

This report presents an overview and discussion of the use of the ambient water quality criterion for methylmercury developed by the U.S. Environmental Protection Agency (EPA) in 2001 (66 FR 1344). Unlike all other previous water quality criteria for the protection of human health, the criterion for methylmercury was issued as a fish tissue concentration (i.e., 0.3 mg methylmercury/Kg wet weight fish tissue), as the fish consumption pathway is the main route of exposure to mercury in the environment. As a result, enforcement of water quality standards based upon this criterion requires either fish tissue sampling or the conversion of the criterion to a concentration in water, especially for the development of National Pollutant Discharge Elimination System (NPDES) permits.

Because many permitted dischargers will be faced with meeting the methylmercury criterion, this report focuses on (1) available analytical methods for evaluating mercury in fish and water;; (2) the proposed methods for translating a fish tissue concentration for mercury into a concentration in water; and (3) implementation of the mercury criterion in the development of Total Maximum Daily Loads (TMDLs) and water quality-based effluent limits (WQBELs). EPA (2002a, 2004a) draft *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* addresses these issues and is discussed below in each relevant section.

Issues regarding mercury are significant because of mercury's complex cycling in the environment, high bioaccumulative potential, and high toxicity. Generally, inorganic mercury is deposited to water bodies through atmospheric deposition (the major pathway), runoff, stormwater discharge, or other industrial or municipal discharges. Once in the water body, mercury deposited in sediments or dissolved in water may be methylated by bacteria to form methylmercury. Methylmercury is highly bioaccumulative and is the form of mercury that is accumulated up the food web. EPA's criterion for methylmercury assumes, therefore, that all mercury in fish is methylated. While this may be true, as discussed in Section 3.1, use of appropriate analytical methods for both total mercury and methylmercury are critical to fully understand site-specific mercury cycling. In addition, as discussed in EPA (2002a) guidance, several methods are available to translate the fish tissue criterion to a water concentration. Although site-specific data may provide the most reliable results, other default options are available, if needed. Finally, EPA (2002a; 2004a) attempts to provide recommendations for using the mercury criterion in the development of TMDLs and WQBELs, and the implementation of these in the NPDES permitting program. Several

different approaches have been used for mercury TMDLs, as no single approach is universally applicable given the site-specific factors that influence mercury deposition, transformation, and accumulation and the nature of the contributing sources to a water body. The approaches that have been taken and their acceptability to EPA, or lack of acceptability, are illustrated with examples.

To address these issues, Section 2 provides a discussion of the analytical methods for evaluating total mercury and methylmercury in fish tissue and water. Section 3 discusses the various methods for conducting a translation of the methylmercury criterion. Section 4 addresses the use of the criterion in developing TMDLs and WQBELs. Finally, Sections 5 and 6 present a discussion of the applicability of the issues to other metals and conclusions/recommendations, respectively. Appendix A provides a bibliography of recent studies that can be used to update default mercury translators. Appendix B describes several mercury TMDLs that are used to illustrate the different approaches.

## **2 Analytical Methods**

Analytical methods to quantify different species of mercury in environmental samples continue to be refined. Section 2 discusses the various methods available for evaluating the forms of mercury in fish tissue and water and reviews factors to consider in selecting an appropriate analytical method.

### **2.1 METHODS FOR EVALUATING TOTAL MERCURY IN FISH TISSUE AND WATER**

For measuring total mercury, EPA Method 1631 can be used on water samples, while EPA Method 747B/SW-846 can be used for solid or semi-solid samples. A brief description of each method, its detection limits, precision, accuracy, and costs is provided below.

#### **2.1.1 Method 1631**

EPA Method 1631 can be used for the determination of total mercury in filtered and unfiltered water (EPA 2002b). Method 1631 is carried out in several steps. First, the various mercury species are oxidized to Hg(II) with bromine monochloride (BrCl). Second, the mercury is reduced to elemental mercury (Hg(0)) with hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) and stannous chloride (SnCl<sub>2</sub>). Third, mercury is purged from the sample onto gold traps for pre-concentration. The gold traps are heated to release the elemental mercury and the detection is performed with cold-vapor atomic fluorescence spectroscopy (CVAFS). Method 1631 has a method detection limit of 0.2 ng/L. This is a performance-based method and actual criteria data are determined before and during analysis. Precision is based on replicate analysis of actual samples and has a limit of 21% RSD (relative standard deviation). Accuracy is determined using National Institute of Standards and Technology (NIST) standards for ongoing precision and recovery (OPR) and matrix spikes/matrix spike duplicates (MS/MSD). OPR samples must fall within 77 – 123% and MS/MSD samples between 71 – 125%. Many laboratories perform this analysis; costs range from \$55 – 200 per sample with a four week reporting time.

#### **2.1.2 Method 7471B/SW-846**

EPA Method 7471B/SW-846 is designed for solid or semi-solid samples, but may also be used for water or aqueous samples, as the analysis portion of this method is covered by EPA Method 245.5 (EPA 1994a). Using this method, solid or liquid samples are digested using a potassium permanganate and acid digestion. The acid digestion ensures that all forms of mercury are oxidized to a water soluble Hg(II) form. The detection is performed using cold-vapor atomic adsorption spectroscopy (CVAAS). In CVAAS the sample is reacted with stannous chloride and the mercury is converted to elemental mercury. The elemental mercury is purged from the sample with nitrogen to an atomic adsorption detector. Typical method detection limits for mercury using this method are 0.2 µg/L. This is a performance based method and actual criteria data are determined before and during analysis. Precision is based on replicate analysis of actual samples although no limits were set in the method. Accuracy is determined using NIST standards for ongoing precision and recovery (OPR) and matrix spikes and matrix spike duplicates (MS/MSD). OPR samples must fall within 90 – 110% and MS/MSD samples between 85 – 115%. Many laboratories perform this analysis and the costs range from \$51 – 200 per sample with a four week reporting time.

### **2.2 METHODS FOR EVALUATING METHYLMERCURY IN FISH TISSUE AND WATER**

The basic method for quantifying methylmercury is EPA Method 1630. Modifications to this method are described in the UW-Madison Standard Operating Procedure (SOP) and the United State Geological Service (USGS) Method.



### 2.2.1 Method 1630

EPA Method 1630 is the main method for quantifying methylmercury in fish tissue and aqueous samples (EPA 2001a), although it has not yet been promulgated. The specific steps in Method 1630 include: 1) distillation to remove the methylmercury from the sample; 2) ethylation to a methylethylmercury form and collection on a graphitic carbon adsorbent trap; and 3) thermal desorption through a gas chromatography column to separate the mercury species before reduction to elemental mercury in a decomposition furnace. The elemental mercury is detected using CVAFS. Method 1630 has a method detection limit (MDL) of 0.02 ng/L (or ng/g) but has the ability to detect as low as 0.009 ng/L.

Also included in this Method is Appendix A for the determination of dimethylmercury. The method for dimethylmercury varies from the original Method 1630 by eliminating the distillation step and purging the entire sample onto the graphitic carbon adsorbent trap. The elemental mercury is separated from the dimethylmercury by using gas chromatography. Two mercury peaks, representing the elemental and dimethylmercury species, are separated in time and are detected by CVAFS. Appendix A for the determination of dimethylmercury has a MDL of 2 pg/L. This is a performance based method and actual criteria data are determined before and during analysis. Precision is based on replicate analysis of actual samples and has a limit of 31% RSD. Accuracy is determined using NIST standards for OPR and MS/MSD. OPR samples must fall within 67 – 133% and MS/MSD samples between 65 – 135%. Several studies have been performed citing the Appendix A method that may be eventually used for validation. In the interim, Appendix A is still considered draft. Unlike EPA Method 1630, the method for dimethylmercury does not specifically discuss how to analyze solids such as fish tissue.

### 2.2.2 UW-Madison SOP

The UW-Madison SOP was developed at the University of Wisconsin-Madison (Hurley et al. 1988). It is virtually identical to Method 1630 with the major exception being the distillation of a larger sample volume, resulting in a lower method detection limit. Copper sulfate is added to the distillation to bind sulfates. This method has a method detection limit of 30 pg/L for methylmercury. The same laboratories that perform Method 1630 could perform this analysis at a cost of approximately \$200 per sample with a four week reporting time.

### 2.2.3 USGS Method

Similar to the UW-Madison SOP, the USGS method is virtually identical to Method 1630 with a slightly larger sample volume used in the distillation (DeWild et al. 2001). Copper sulfate is also added to the distillation to bind sulfides. The USGS method has a MDL of 40 pg/L for methylmercury. The same laboratories that perform Method 1630 could perform this analysis and the cost is approximately \$200 per sample with a four week reporting time.

## 2.3 CLEAN HANDS SAMPLING

EPA Method 1669 covers the sampling and preservation of samples using clean hands techniques (EPA 1996a). Specifically, the method details the procedures for collecting water samples using a two person team, wherein one person becomes the “clean hands” sampler, while the second person, the “dirty hands” sampler, is available to operate equipment and perform tasks where contamination may be present. Procedures such as preparation of blanks, duplicates, spikes, sample filtration, and preservation are described in this method.

## 2.4 CONSIDERATIONS IN THE SELECTION OF AN ANALYTICAL METHOD

The selection of a method to test for either total mercury or methylmercury should be based on several factors, including method detection limit, validity of the method, and quality control procedures. These factors determine the quality and usability of the generated data. Without specific quality assurance (QA) criteria, comparison between samples and matrix interference may not be possible. Similarly, if QA criteria are too wide, the results may be highly variable between samples. Tighter QA criteria allow the generation of higher quality data.

The MDL is determined by the actual method used to analyze mercury. For example, methods using atomic fluorescence have a lower MDL than atomic adsorption for the determination of total mercury. In particular, atomic fluorescence has a broader linear dynamic range and greater sensitivity than atomic adsorption.

In comparison to total mercury methods, methods for methylmercury are still experimental and have not been fully validated by EPA. Indeed, many more studies have been performed on development and validation of total mercury methods compared to methylmercury, due to greater interest by EPA and industry. Methylmercury analysis is typically performed on fish tissue to better understand bioaccumulation of mercury and determine the partitioning between total mercury and methylmercury.

Similarly, many laboratories are capable of running both EPA Methods 1631 and 7471B for total mercury and have developed competitive services to support this need, including well developed quality assurance/quality control (QA/QC) procedures. In contrast, there are only a few laboratories capable of performing methylmercury analysis. As a result, most analytical laboratories have not developed methods for methylmercury analysis as a routine service. Prior to analyzing samples for methylmercury, it is critical to ensure that the laboratory has the capability to generate results that meet QA/QC standards.

### **3 Translators Issues**

This section discusses EPA's draft guidance and evaluates the available options for establishing site-specific translators. Translation of EPA fish tissue criterion into a water column concentration will typically be necessary when developing water quality-based effluent limits. However, in some cases, it may not be necessary to translate EPA's fish tissue methylmercury criterion to a water quality criterion (EPA 2004a). For example, if elevated mercury concentrations in fish are due primarily to atmospheric or other non-point inputs, point source dischargers may simply be required to maintain mercury levels in effluent at or below current levels (see Section 4).

#### **3.1 OVERVIEW OF TRANSLATIONS WITHIN AND BETWEEN MEDIA**

Conceptually, the translation from methylmercury in fish to total mercury in water can be viewed as a single step (i.e., direct method) or a multi-step process, as shown in Figure 1. In the direct method, total mercury in fish is directly translated to total mercury in water. In contrast, the multi-step approach (methylmercury in fish to dissolved methylmercury in water to total mercury in water) reflects the fact that in water, methylmercury is much more bioaccumulative, and dissolved methylmercury is much more bioavailable than particulate mercury. In addition, translation from methylmercury in fish to total mercury in fish may also be implemented, since total mercury is easier and less expensive to measure. However, even the inclusion of various intermediate steps in the translation process is actually a gross oversimplification of the very complex processes of mercury bioaccumulation. From an implementation perspective, it often may be more practical to collapse the translation into a simple ratio between readily measurable endpoints, namely total mercury in fish and water (see Section 3.3).

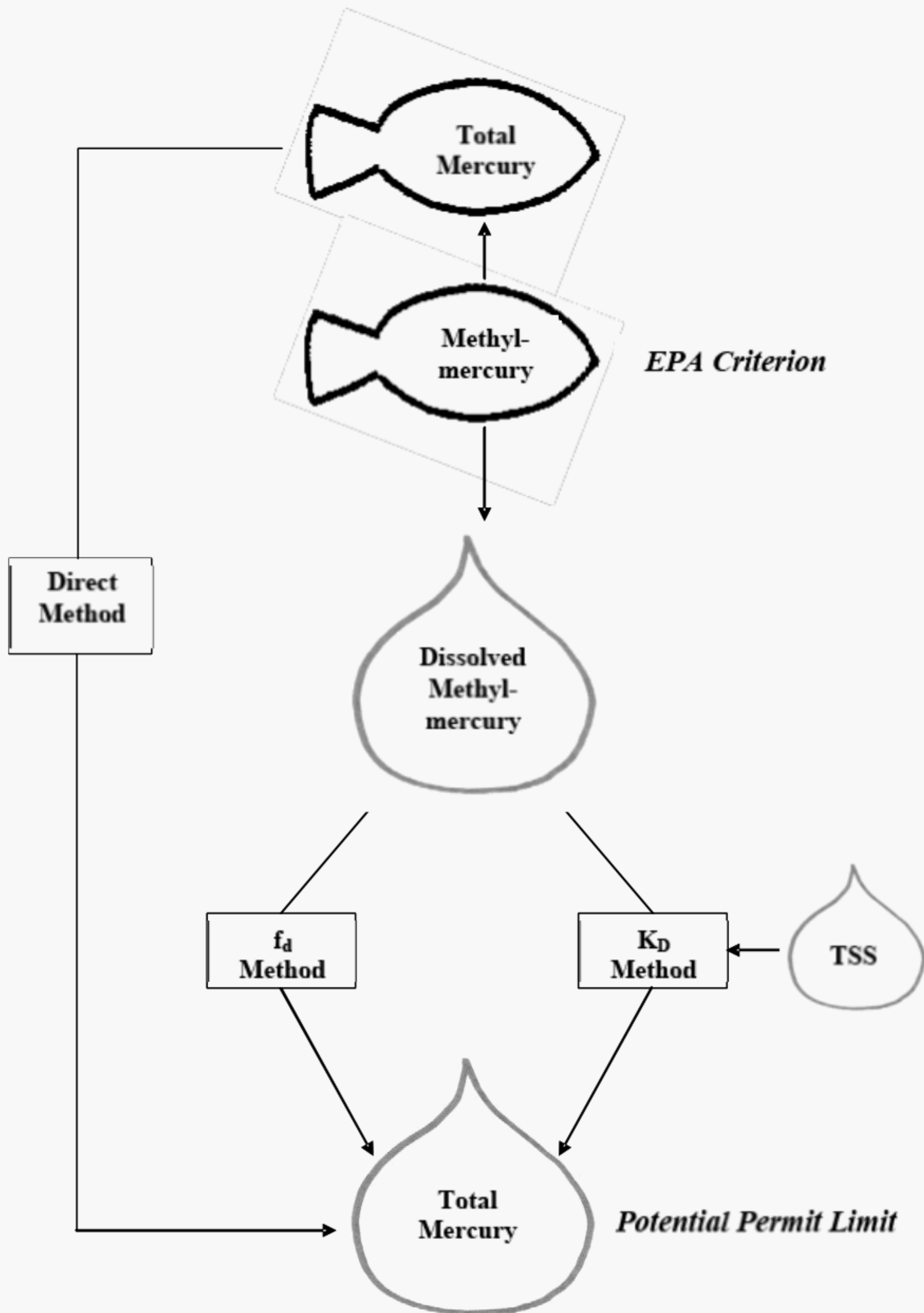


Figure 1—Conceptual Overview of Mercury Translations



The major challenge in developing mercury translators is the enormous variability in the site-specific potential for mercury methylation and bioaccumulation. This is illustrated in Figure 2, which compares unfiltered methyl- and total mercury data collected nationwide by the U.S. Geological Survey as part of the National Water Quality Assessment (NAWQA) program (Krabbenhoft et al. 1999). While there is a clear trend of increasing methylmercury concentrations with increasing total mercury, any given total mercury concentration could be associated with methylmercury levels ranging over two orders of magnitude. With another order of magnitude variation in the prediction of fish tissue concentrations from aqueous methylmercury concentrations (Brumbaugh et al. 2001), it is clear that the significance of a particular total mercury concentration in water is highly uncertain. Among the important factors that contribute to the variability in mercury bioavailability and bioaccumulation are pH, dissolved organic carbon (DOC), salinity, water flow (i.e., streams versus lakes, lake flushing rate), temperature, redox potential, sulfide and sulfate, suspended solids, nutrient loading, fish age and size, prevalence of wetlands and forested land cover in the watershed, and concentration-dependent demethylation (Brumbaugh et al. 2001; Qian et al. 2001; Kamman et al. 2004; Marvin-DiPasquale et al. 2000; Sonesten 2003a; Rose et al. 1999; Ullrich et al. 2001; Watras et al. 1998).

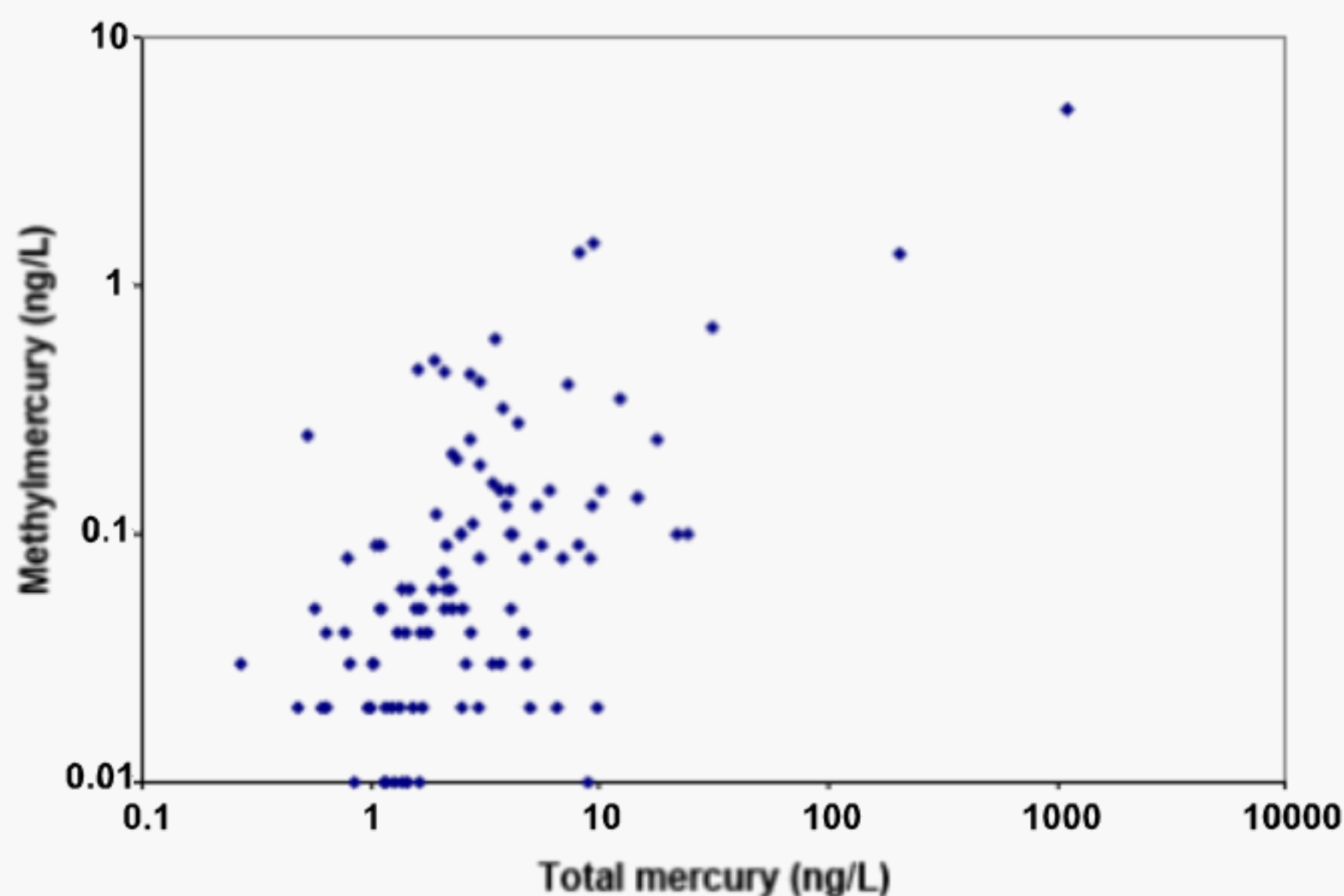


Figure 2—Total Mercury versus Methylmercury in Stream Water Samples Collected Throughout the United States as Part of the NAWQA Program

EPA (2000a,b) compiled information on mercury ratios within and between media, as summarized in Table 1. These data provide an overview of the central tendency and range of the various ratios. Reasonably robust data sets were compiled for freshwater systems, including lentic (lake and reservoir) and lotic (stream and river) systems. Estuarine data were found to be very limited, and marine data were not compiled.

Table 1—Summary of Key Mercury Ratios within and Between Media, as Compiled by EPA (2000a,b)

Ratio	Aquatic System <sup>a</sup>	Geometric Mean <sup>b</sup>	Range <sup>b</sup>	Number of Values <sup>c</sup>
Trophic level 4 fish methylmercury : aqueous dissolved methylmercury (BAF)				
	Lakes	5,740,000	2,800,000 – 11,800,000	8
	Rivers	1,240,000	73,400 – 20,900,000	7
	National	2,670,000	250,000 – 28,400,000	15
Trophic level 3 fish methylmercury : aqueous dissolved methylmercury (BAF)				
	Lakes	1,115,000	423,000 – 2,930,000	7
	Rivers	517,000	46,000 – 5,820,000	25
	National	680,000	74,300 – 6,230,000	32
Dissolved methylmercury as a fraction of total mercury in water (f <sub>d</sub> )				
	Lakes	0.032	0.002 – 0.139	9
	Rivers	0.014	0.002 – 0.051	13
	Estuaries <sup>d</sup>	0.19	0.185 – 0.195	2

a. Bioaccumulation factors (BAFs) were not derived for estuarine systems due to lack of data.

b. Values are based on the combined direct measurements and converted values presented by EPA (2000a,b). Ranges presented for BAFs represent 5th and 95th percentiles.

c. Each “value” is an average for a species at a particular site. In some cases, multiple water bodies and/or species evaluated in a single study were aggregated.

d. The higher values for estuaries appear to be associated with the limited data set. Elevated salinity reduces methylation and mercury bioaccumulation.

The ratios summarized above were developed based on a literature review performed during the late 1990s. Numerous studies published since that time contain extensive additional data for freshwater, estuarine, and marine systems. Selected studies containing relevant data are listed in Appendix A. While the newer data for freshwater systems appear generally consistent with the information compiled by EPA (2000a,b), a detailed comparison was not conducted for this report. The large volume of data now available merits consideration by EPA or others, to develop a better understanding of BAF and fraction dissolved (f<sub>d</sub>) values in estuarine and marine systems, and to further refine the current understanding of these parameters in freshwater systems.

In addition to the ratios shown in Table 1, the ratio of methylmercury to total mercury in fish is important to the development of mercury translators. The draft EPA guidance indicates that essentially all of the mercury in edible fish tissue can be assumed to be present as methylmercury (EPA 2004a). This assumption is based on a landmark paper by Bloom (1992), which argued that earlier estimates of a lower proportion of methylmercury in fish muscle were due to analytical artifacts. Sources of artifactual results were identified as (1) contamination of samples with inorganic mercury, especially prior to development of “ultra-clean” sample handling methods; (2) incomplete homogenization of samples combined with rounding down of excessively high values to 100%; and (3) incomplete recovery in methylmercury methods versus near-complete recovery in total mercury methods. Subsequent research has generally confirmed this finding, at least for higher trophic level (carnivorous) fish in waters relatively uncontaminated with inorganic mercury (Lasorsa and Allen-Gil 1995; Wagemann et al. 1997). Where slightly lower percentages of methylmercury have been measured in fish muscle (e.g., Kannan et al. 1998; Neff 2002), it is difficult to refute a possible role of incomplete analytical recovery of methylmercury. However, the results of Baeyens et al. (2003) provide a clear counter example. Specifically, methylmercury comprised only 58% of the total mercury in commercial fish captured from the Scheldt estuary in Belgium, although the same species captured from the Belgian coastal zone and the Greater North Sea contained primarily methylmercury as expected (approximately 90% or greater). The authors speculate that the Scheldt fish may feed at a lower trophic level due to the presence of large amounts of untreated sewage (Baeyens et al. 2003). Despite this apparently unexpected finding, the uncertainty associated with an assumption of 100% methylmercury in edible fish tissue can generally be considered low relative to the other uncertainties associated with criteria translation between fish and water.

Finally, while mercury in fish consumed by humans is essentially all methylmercury, this is not necessarily the case for fish consumed by wildlife. In contrast to humans, wildlife consume whole fish and typically consume smaller (lower trophic level) fish. Methylmercury constitutes less than 100% of total mercury in whole fish and in the muscle tissue of some lower trophic level fish (Bloom 1992; EPA 2000a). Comparison of the human and wildlife values developed by EPA as part of the Great Lakes Initiative suggests that piscivorous wildlife may actually be more sensitive to mercury than humans (EPA 1995). If water quality criteria are developed specifically for the protection of wildlife, then the ratio between methylmercury and total mercury in whole fish would merit further evaluation.



## 3.2 EPA PROPOSED TRANSLATION METHODS

The draft EPA guidance recommends the following approaches to criteria translations, in order of preference: (1) derive site-specific BAFs, (2) use a bioaccumulation model, or (3) use EPA's national default translators (EPA 2004a). Site-specific methodologies (i.e., EPA's preferred approach) are discussed further in Section 3.3. Bioaccumulation models and default translators are addressed below.

### 3.2.1 Bioaccumulation Models for Mercury

EPA (2004a) does not recommend any specific bioaccumulation models for mercury, although a modeling approach is ostensibly preferred over the use of default translators. Despite extensive study, there are no accurate, nationally applicable models for predicting mercury bioaccumulation. Models developed for hydrophobic organic chemicals are not directly useful for this purpose, although conceptual modifications to address speciating chemicals such as mercury have been suggested (Toose and Mackay 2004). As noted by EPA (2004a), even the Mercury Cycling Model (Tetra Tech 1999) does not predict bioaccumulation, but rather uses BAF as an input. Along the same lines, Hope (2003) developed an elaborate, probabilistic food web model for mercury in conjunction with TMDL development for the Willamette River in Oregon. However, critical components such as the ratio of methyl- to total mercury in surface water and bioaccumulation factors at the base of the food web were based on site-specific empirical data. As a result, this type of model is not transferable to other waterways without extensive data collection. Furthermore, the model assumes that site-specific  $f_d$  and BAF levels are independent of total mercury loading, which may not be valid (Marvin-DiPasquale et al. 2000; Schaefer et al. 2004); thus without further validation over time, this model cannot substitute for continued direct sampling of fish tissue.

As an alternative to process-based or mechanistic mathematical models, the draft EPA guidance suggests that regression models incorporating such variables as pH, DOC, and fish age may be acceptable for criteria translation purposes. According to EPA's *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (EPA 2000c), such models should predict bioaccumulation based on the most biologically relevant chemical form (e.g., dissolved methylmercury), while also allowing for translation between the bioavailable form and the total concentration in water. Recent efforts to develop nationally applicable regression models have not produced highly accurate results, although they are probably more accurate than national default BAFs. Brumbaugh et al. (2001) used data from the NAWQA program to develop a model predicting total mercury in fish (normalized to fish length) based on methylmercury concentrations in water (unfiltered). The most useful parameters in reducing variability in the model were pH, percent wetlands in the watershed, and acid volatile sulfide (AVS) in sediment. However, the model explained only 45% of the variation in fish tissue concentrations. Ongoing studies through NAWQA and other programs (e.g., Brigham et al. 2003) may eventually lead to improvements in the ability to model mercury bioaccumulation in stream ecosystems.

Regression models developed using regional data sets from lake sampling programs have provided greater accuracy than the NAWQA example cited above. Several examples are discussed below.

- *Canadian lakes:* Moore et al. (2003) were able to explain 80% of the variability in mercury bioaccumulation among 38 Canadian lakes based on pH, DOC, and methylmercury in water. However, when this model was applied to a subset of the NAWQA stream data, only 32% of the variation was explained. The limited applicability of the Moore et al. (2003) model to the NAWQA data is likely due to differences between lake and stream systems as well as regional geological differences. It is clear that mercury methylation is more variable over time in streams as compared to lakes. In an evaluation of within-site variability, Kelly et al. (1995) found significant correlations between total and methylmercury in water only for lakes and not for streams.
- *Swedish lakes:* Hakanson (2000) assessed mercury concentrations in fish collected from 39 Swedish lakes. His regression model explained 85% of the observed variation based on the following variables: lake morphometry (?area/depth), mercury in sediment, pH, phosphorus, and lake depth. Hakanson (2000) proposes that the model can assist in the development of lake remediation strategies but cautions that it should not be applied to reservoirs or to lakes in different climatological zones.
- *New Hampshire and Vermont lakes:* Another example of regional modeling for lake systems is a model developed by Kamman et al. (2004) for lakes in New Hampshire and Vermont. Interestingly, this model did not include any measure of mercury concentrations in water. Instead, data on acid neutralizing capacity, DOC, pH, conductivity, and lake flushing rate were used to generate binary predictions as to whether or not yellow perch



fillets would contain greater than 0.3 µg/g total mercury. With an error rate of only 13%, this model was quite accurate; however, it would not meet the requirements for BAF models laid out by EPA (2000c).

On a cautionary note, Sonesten (2003a,b) argues that multiple linear regression, the method used by Moore et al. (2003) and Hakanson (2000), is mathematically inappropriate for assessing mercury bioaccumulation. Due to intercorrelation among environmental variables, multiple linear regression may overstate the amount of variation explained and could potentially lead to incorrect identification of key environmental factors affecting bioaccumulation. Sonesten (2003a,b) advocates the use of partial least squares regression, but this method does not produce a predictive equation that could be used for purposes of mercury translator development.

With these caveats, regionally applicable models for lake systems may provide a viable option for mercury criteria translation purposes, if available for a particular lake of interest. In addition to the models described above, models are also available for reservoirs (Braga et al. 2000), utilizing explanatory variables such as area flooded, reservoir age, and the ratio of catchment area and runoff (French et al. 1998; Jin et al. 1999; Therriault and Schneider 1998). However, accurate models are not yet available for river systems, and it appears that mercury bioaccumulation modeling has not been attempted in estuarine or marine systems (Braga et al. 2000). Thus, bioaccumulation models for criteria translation in these systems will need additional research before being useful for NPDES or TMDL regulations.

### 3.2.2 National Default Translators

The draft EPA guidance includes empirically derived default values to simplify the translation from the fish tissue methylmercury criterion to a water quality criterion for total mercury. Two sets of values are provided: (1) BAFs describing the relationship between dissolved methylmercury in water and methylmercury in fish, and (2) fraction dissolved ( $f_d$ ) values describing the relationship between total mercury and dissolved methylmercury in water. In addition, partition coefficients ( $K_D$  values) that account for the role of total suspended solids (TSS) in determining dissolved mercury concentrations are described, although default values are not identified in the draft guidance.

The recommended default BAFs are central tendency values developed from the data summarized in Table 1. Separate BAFs are provided for trophic level 3 (e.g., yellow perch, bluegill), and trophic level 4 (e.g., bass, walleye). However, the distinction between lentic, lotic, and estuarine systems is not preserved in the national default BAFs. In contrast, separate lentic and lotic  $f_d$  values are provided. Like the BAFs, the recommended default  $f_d$  values represent the central tendency of the available data. The BAF and  $f_d$  values can be used to calculate a total mercury water quality criterion from a methylmercury fish tissue criterion as follows:

$$\text{Water quality criterion} = \frac{\text{Fish tissue criterion}}{\text{BAF} \times f_d}$$

The proportion of fish consumed from different trophic levels must be determined in order to identify a weighted-average BAF for use in this equation. EPA did not identify default values for the fraction of fish consumed from different trophic levels as part of the draft guidance.

An example of a translator is provided by the Middle and Lower Savannah River Mercury TMDL (EPA, 2001b). This TMDL, further discussed in Appendix B, has been withdrawn but remains cited by EPA as an example of a mercury TMDL. The fish tissue criterion was 0.4 mg/kg in this example. Site-specific data were used to select the BAF, which was 4,000,000, and the  $f_d$ , which was 0.0353. Fish were sampled in the basin during the late summer of 2000, targeting largemouth bass (trophic level 4). The data indicated BAFs ranged from <1,000,000 to > 8,000,000. The BAF used in criterion derivation was selected from the central tendency of the data for fish 315 mm in length, which was considered to be most representative of the size of fish most likely to be consumed. The  $f_d$  value represented the median of data from across the watershed. Thus, the water quality criterion was 2.8 ng/L, as follows:

$$\text{Water quality criterion} = \frac{0.4 \text{ ppm}}{4,000,000 \times 0.0353} = 0.0000028 \text{ ppm}$$

The EPA draft guidance also refers to  $K_D$  values. The  $K_D$  approach is intended to reduce uncertainty by accounting for mercury partitioning to TSS; however, the recommended default values are not provided, and the equations

describing  $K_D$  application are incorrect.<sup>1</sup> Equations 6 and 7 in the draft guidance (EPA 2004a) should read as follows:

$$K_D = \frac{C_{Hg,p}}{C_{MeHg,d} \times TSS} \quad (\text{Equation 6})$$

and

$$f_d = \frac{1}{1 + (K_D \times TSS)} \quad (\text{Equation 7})$$

where

- $K_D$  = partition coefficient for dissolved methylmercury to particulate mercury (L/mg);
- $C_{Hg,p}$  = concentration of particulate total mercury (mg/L);
- $C_{MeHg,d}$  = concentration of dissolved methylmercury (mg/L);
- $f_d$  = fraction of total mercury present as dissolved methylmercury (unitless); and
- TSS = total suspended solids (mg/L)

Note that there are multiple definitions of  $K_D$ , depending on which form of mercury is of interest. The  $K_D$  described here is also referred to as a “pseudo”-  $K_D$ , because it relates the total and dissolved concentrations of two different forms of mercury. Using this “pseudo”-  $K_D$  approach, EPA (2000b) derived default log  $K_D$  values for lentic and lotic systems of 6.83 and 6.44, respectively.

Although the  $K_D$  approach is intended to reduce uncertainty by accounting for TSS concentrations, it is important to understand that the  $K_D$  itself is not actually a constant.  $K_D$  values vary with TSS concentrations, because of mercury partitioning to colloids (solids not captured during sample filtration due to their small size) (Babiarz et al. 2001; EPA 2000b). Further, Lindstrom (2001) found that in addition to TSS,  $K_D$  values in Swedish lakes were also influenced by iron concentrations and the ratio of drainage area to lake area, probably due to differential partitioning to different types of solids. On the other hand, the  $f_d$  approach is also highly variable. For instance, due to concentration-dependent demethylation processes,  $f_d$  is inversely related to total mercury concentrations, both within and among aquatic systems (Marvin-DiPasquale et al. 2000; Schaefer et al. 2004). Seasonal variability is also well documented (Babiarz et al. 1998; Balogh et al. 2002; Kelly et al. 1995). In the methylmercury criteria document (EPA 2001b), EPA declined to state whether the  $f_d$  or  $K_D$  approach would be preferable, stating that “perhaps the approach taken should be the one with the stronger data base.” No evaluation of the relative merits of the available data is provided in the draft implementation guidance. To make the guidance most usable, EPA should evaluate the available data to determine whether the  $K_D$  approach reduces the variability within and among sites compared to the  $f_d$  approach. No such evaluation has been conducted, and therefore, it is not possible to determine which approach is preferable.

At a broader level, EPA’s current methodology fails to identify whether the use of two layers of default values (dissolved methylmercury BAFs and  $f_d$  values) results in unnecessary uncertainty. This issue is important because the use of multiple steps in criteria translation leads to the propagation of uncertainty (Taylor 1982), potentially causing a two-fold error (approximately) in the final criterion (AMEC and ENVIRON 2003). Additionally, there is evidence that methylmercury BAFs and  $f_d$  values may be inversely related, rather than independent as generally assumed. When the NAWQA sampling sites were examined based on surrounding land use, the land use types having the highest mercury levels in fish and the highest percentage methylmercury in water also had the lowest methylmercury BAFs (Brumbaugh et al. 2001). The implications of this relationship should be fully examined before using national default translators at sites. Such an evaluation could be accomplished by calculating total mercury BAFs from the available data for comparison with the two-step translation approach.

<sup>1</sup> Rather than citing the proper definition of the  $K_D$  value of interest in Equation 6, the authors of the draft guidance cited a “short-cut” equation used for back-calculation purposes in the original source document (EPA 2000b, p. 5). That equation contained a typographical error (compare to Appendix A of EPA 2000b which appears to be correct), which led to further confusion regarding the application of the  $K_D$  value (Equation 7).



At the broadest level, it must be recognized that the national default values have a high probability of being significantly inaccurate at any given site. As discussed above, appropriate translators from mercury in fish to total mercury in water would be expected to vary among sites by several orders of magnitude. Since the national BAFs do not distinguish between lentic and lotic systems, they are likely to be over-protective for streams and rivers and under-protective for lakes and reservoirs. Acidic lakes and recently flooded reservoirs (i.e., flooded within the last 20-30 years) are particularly susceptible to mercury bioaccumulation (Bodaly et al. 1997; Gilmour and Henry 1991) and probably would not be adequately protected by the national default translators. Conversely, the default values are likely to be particularly over-protective for estuarine and marine systems, where mercury bioaccumulation is lower (Neff 2002; Ullrich et al. 2001). The draft EPA guidance clearly states that the national default values are only “first-phase estimates of water column targets” and should be replaced with site-specific information if available (EPA 2004a). However, if national default values are to be used to target sites for further investigation, the efficiency of investigation programs would be improved if EPA were to adopt more specific default values for different types of aquatic systems. Incorporation of recent data such as that cited in Appendix A would facilitate achievement of this goal.

### 3.3 SITE-SPECIFIC TRANSLATORS

The preferred approach to criteria translation, as recommended by EPA, is the use of site-specific translators. Provided that the study design accommodates an expectation of high variability, it should be possible to effectively develop site-specific translators for mercury. Kelly et al. (1995) called into question the technical feasibility of identifying site-specific translators for lotic systems, reporting no relationship between aqueous total and methylmercury concentrations over time, either within or among stream sites. However, their data show that despite high variability, it was possible to distinguish between sites with different average levels of mercury methylation. Similar studies evaluating within-site variability in methylmercury BAFs over time are not available. The results of NAWQA monitoring studies are somewhat promising, however, considering that variation among multiple sites nationwide was less than an order of magnitude, when fish size and species difference were accounted for (Brumbaugh et al. 2001). Within-site variation should be considerably lower.

All site-specific studies of mercury bioaccumulation should use ultra-clean sampling and analytical techniques, to avoid trace-level contamination. Fish length should always be measured, and fish weight and age determination are also desirable. Fish tissue concentrations may be normalized to a constant fish length as part of BAF development (e.g., Brumbaugh et al. 2001; Tremblay et al. 1998). A corollary of this requirement is that individual fish should not be composited for analysis unless they are essentially identical in size. Multiple water and fish tissue samples should be collected over time to account for seasonal and interannual variation in mercury concentrations. Fish tissue concentrations integrate exposure over time and exhibit little seasonal fluctuation (Foster et al. 2000), whereas water samples provide only a snapshot of fluctuating mercury concentrations, especially in lotic systems (Balogh et al. 2002, 2004). Therefore, water samples may be collected with greater frequency than fish tissue samples, in order to provide data for estimating average aqueous exposure levels.

The first step in developing a site-specific study design is to define the spatial boundaries of the area where the site-specific water quality criterion is to apply. Next, several key questions must be addressed, as follows:

- *Where do people catch fish within the study area and which fish do they eat?* The answer to these questions will determine which fish species are targeted for analyses and where they are sampled. Although a formal creel survey would provide the most definitive information, a less rigorous approach will generally suffice. Information on the species composition of the local fish community, identification of access points, and an understanding of regional fish consumption preferences can be used to estimate local consumption patterns. From this information, a reasonable number of target species can be selected. Data recently compiled by EPA (2004b) comparing average mercury concentrations among species should be helpful in assuring that the target species are representative of other potentially consumed species, in terms of their bioaccumulation potential. The average size of fish consumed should also be considered, to guide sample collections. Site-specific fish consumption rates are also relevant if the fish tissue criterion is to be adjusted on a site-specific basis; however, such adjustments of EPA fish tissue criterion are beyond the scope of this report.
- *Are there habitat differences within the study area that could affect mercury bioaccumulation?* This question is important in determining whether multiple subareas should be separately evaluated. For instance, bioaccumulation may differ between tributary streams, mainstem rivers, impoundments, and wetlands. Sub-basins of larger lakes can also exhibit differences in mercury bioaccumulation (AMEC and ENVIRON 2003).

- *Is there a need or motivation to understand the site-specific mechanisms underlying any variations in bioaccumulation potential over space and time?* Although the draft EPA guidance focuses on methylmercury BAFs and  $f_d$  values, it also states that site-specific BAFs may be developed that directly relate total mercury concentrations in water and fish tissue. While limiting the analyte list to total mercury certainly reduces the cost per sample, it also limits to some degree the ability to interpret the results including the ability to identify potential mercury sources. Southworth, et al. (2002) describe a post-remediation monitoring program where measurement of methylmercury was important to understanding apparently anomalous results. However, such a detailed understanding may not be necessary in all cases. Where limited resources preclude extensive methylmercury analyses, a simpler total mercury assessment may be more defensible than the use of national default values.

Clearly, the scope and cost of site-specific translator development will vary considerably among sites. While the decision about the number and types of samples to take will be a judgment call made between risk managers and dischargers, to illustrate a range of options, two hypothetical scenarios are described below. In the first scenario, the study area is assumed to be relatively homogeneous with regard to habitat types, and risk managers determine that it is not necessary to develop a mechanistic understanding of site-specific bioaccumulation. In the second scenario, multiple habitat types are present, and the potential for future remedial actions dictates a more detailed understanding of bioaccumulation mechanisms.

In the first scenario, two target species are selected from the list of potentially consumed fish species. Based on the data set of average mercury concentrations compiled by EPA (2004b), largemouth bass and bluegill sunfish are selected as representing high and medium bioaccumulation, respectively. Three sampling stations are identified based on locations of public access to the water body. A two-year study is undertaken to address interannual variability. Fish tissue samples are collected twice per year, in spring and fall, to encompass seasonal variability. Thus, a total of 24 fish tissue samples are collected (2 species x 3 locations x 4 sampling events). For surface water analyses, sampling is conducted every other month, and the results for each six-month period are averaged for comparison to the fish tissue data collected at the end of that time. Also, because fish are mobile, water samples are collected upstream, adjacent to, and downstream of each fish sampling station. A total of 108 water samples are collected (9 locations x 12 sampling events). All samples (i.e., fish tissue and surface water) are analyzed for total mercury only. Analytical costs for this scenario are estimated in Table 2.

Table 2—Estimated Laboratory Costs for Mercury Sampling—Scenario 1

Analysis	Cost per sample*	Number of samples	Total cost
Total mercury in tissue	\$115	24	\$2,760
Total mercury in water	\$85	108	\$9,180
Grand total			\$11,940

\*Will vary depending on the specific laboratory selected to perform the analysis.

This cost estimate is intended to provide a general sense of the investment needed to develop a relatively simplistic site-specific mercury translator. Costs associated with sample collection would be site-specific and are not estimated here. The cost of analyzing QC samples (duplicates, blanks) also is not included.

In the second scenario, separate translator development is undertaken for a river upstream of an impoundment, the impoundment itself, and the river downstream of the impoundment. Within each of these subareas, the number of target species and the frequency of sampling is the same as in the first scenario. However, the number of fish sampling stations per subarea is reduced to two, with three water sampling locations again associated with each fish sampling station. The analytical program is greatly expanded compared to the first scenario, in an attempt to capture various environmental variables that could be key to understanding differences in bioaccumulation between subareas or over time. In addition to several surface water parameters, a limited sediment sampling component is included, because some investigators have found sediment organic carbon and sulfide content to be correlated with mercury bioaccumulation (e.g., Brumbaugh et al. 2001). Sediment samples are collected at the same locations as the water samples and at the same frequency as the fish tissue samples, for a total of 72 sediment samples (3 subareas x 6 locations per subarea x 4 sampling events). While fish tissue samples are still analyzed only for total mercury, water samples are also analyzed for dissolved methylmercury and a variety of parameters that have been found to be correlated with bioaccumulation potential in published studies. A field probe is used to measure pH, temperature, and conductivity in conjunction with surface water sampling. Approximate analytical costs for this scenario are



shown in Table 3, below. As in the first scenario, costs associated with sample collection and QC analyses are not included.

Table 3—Estimated Laboratory Costs for Mercury Sampling—Scenario 2

Analysis	Cost per sample*	Number of samples	Total cost*
<b><i>Fish tissue</i></b>			
Total mercury	\$115	48	\$5,520
<b><i>Surface water</i></b>			
Total mercury	\$85	216	\$18,360
Dissolved methylmercury	\$200	216	\$43,200
DOC	\$35	216	\$7,560
TSS	\$15	216	\$3,240
Sulfate	\$18	216	\$3,888
Sulfide	\$30	216	\$6,480
Total iron	\$30	216	\$6,480
<b><i>Sediment</i></b>			
Total organic carbon	\$40	72	\$2,880
AVS	\$75	72	\$5,400
Grand total			\$103,008

\*Will vary depending on the specific laboratory selected to perform the analysis.

A potentially workable hybrid between these two scenarios would be to analyze only a subset of surface water samples in the second scenario for the constituents in Table 3. This approach could reduce analytical costs nearly by half, while preserving the ability to understand the factors contributing to variations in mercury bioaccumulation.

Both scenarios provide sufficient data to identify total mercury BAFs, allowing the most direct method of site-specific mercury criteria translation. The primary practical advantage of the second scenario is that it provides a baseline data set for interpreting future fish tissue data. For instance, if actions to reduce mercury concentrations in fish are not uniformly successful, the baseline data would support an analysis of the cause(s) of the observed discrepancy.

## 4 Use of Translators in TMDL and Permit Limit Calculations

Section 4 provides information on calculating TMDLs and permit limits using the methylmercury water quality criterion. A critical piece of the TMDL and permit limit determination for mercury is determining compliance with the either a concentration of mercury in fish tissue or water. As a result, many of the issues discussed in Section 3 are also applicable to TMDLs and permit limits. Specific approaches to using the methylmercury criterion in determining TMDLs and permit limits as well as recommendations for obtaining a realistic mercury permit limit are presented below.

### 4.1 INTRODUCTION TO WQBELS AND TMDLS

This section provides a brief overview of the concepts and terminology needed to understand how mercury translators can be applied to the calculation of permit limits. This overview is based upon information in various EPA publications (EPA 1991a; 1991b; 1994b; 1996b; 1999).

The Federal Water Pollution Control Act Amendments of 1972 (also known as the Clean Water Act [CWA]) established the NPDES for permitting point source discharges of pollutants to surface waters. NPDES permits contain effluent limitations, which can be based upon both the technology available to control pollutants (technology-based effluent limits) and levels needed to be protective of the water quality standards of the receiving water (WQBELs). Where technology-based limits are not sufficient to ensure that water quality standards will be met, the CWA and NPDES regulations require more stringent WQBELs.

WQBELs reflect an integrated approach designed to protect aquatic life and human health from adverse effects due to the release of toxic pollutants. WQBELs are based upon water quality standards, which states are required to develop under Section 303(c) of the CWA. Water quality criteria, such as the criterion for methylmercury, are legally applicable only when they are incorporated into a state's water quality standards. A water quality standard (WQS) also includes a description of the designated use of the water body and antidegradation provisions, which is important because if the designated use changes, the criterion may cease to be applicable.

In determining whether WQBELs are needed to protect water quality, a permit writer must determine whether the discharge causes, or has the reasonable potential to cause, or contributes to, an excursion of numeric or narrative water quality standards (40 *CFR* §122.44(d)(1)). Usually, reasonable potential is determined based upon effluent monitoring data, using a statistically determined worst-case concentration in the effluent to calculate a projected in-stream concentration under critical stream conditions. If the projected in-stream concentration exceeds the water quality criterion, WQBELs are required. Reasonable potential can also be determined without facility-specific monitoring data, but WQBELs derived in this manner are more readily challenged.

The permit limits for a facility reflect the wasteload allocation (WLA) for that particular point source. In other words, the effluent limitations in the permit are established so that the facility will not exceed its allocation (expressed in terms of mass per day). The WLA is determined through water quality modeling, which may range from simplistic to complex, and may or may not include a mixing zone allowance, depending upon the State and upon the pollutant. A simple steady-state model consists of a mass balance equation using single, constant inputs for effluent flow, effluent concentration, background receiving water concentration, receiving water flow, and meteorological conditions. Dynamic models, which account for an array of variables that impact pollutant fate and transport, calculate a probability distribution for receiving water concentrations rather than a single, worst-case concentration. The WLA for each applicable pollutant is eventually translated into maximum daily and average monthly permit limits, using statistical approaches (EPA 1991a).

The WLA is used in TMDLs to determine the fraction of the allowable receiving water load that is allocated to one of the point sources. A TMDL is an estimate of the maximum amount of a specific pollutant that a body of water can assimilate or transport without violating water quality standards. The TMDL includes loadings from point sources, nonpoint sources and natural background, some margin of safety, consideration of seasonal variability, and potentially allowances for future increases in pollutant loads. Although the TMDL process provides a mechanism for integrating both point and nonpoint pollutant sources into a single evaluation, characterization and control of point sources is much easier compared to nonpoint sources.

## 4.2 LISTING ISSUES THAT TRIGGER TMDLS

Under Section 303(d) of the CWA, states are required to submit to EPA a list of all water bodies that do not meet water quality standards, (i.e. are impaired). A water body is also considered impaired when one or more designated uses are not met, including aquatic life uses, recreational uses, public water supply, and fish consumption. Most often, fish consumption is the category that results in an impairment for mercury or other bioaccumulative chemicals. TMDLs are required for each combination of impaired water and pollutant causing the impairment.

When determining impairment, a state is to consider “all relevant data and information that are consistent with its assessment methodology” (EPA 2003a). The types of data that can be used by states to assess whether fish and shellfish consumption-based water quality standards are attained include chemical data, fish consumption advisory information, shellfish growing area classifications, and bacteria criteria; however, only chemical data and fish consumption advisory information are applicable to mercury or other bioaccumulative chemicals. The three types of chemical data that may be used are concentrations in fish tissue, concentrations in the water column, and concentrations in sediment. Most states directly monitor tissue concentrations, but some states examine water column and/or sediment samples. Although analysis of water samples is less expensive, tissue data integrates the wide fluctuations in water column concentrations that can occur over time, and can be directly used to calculate human health screening values. Analysis of sediment concentrations may provide more accurate information where the chemical is metabolized in fish tissues (e.g., polycyclic aromatic hydrocarbons [PAHs]).

States can also use fish consumption advisory information developed by health or environmental agencies as the basis for deciding whether water quality standards are met. Fish consumption advisories, which are not regulations, inform the public about limiting consumption of individual fish species from certain water bodies.

In October 2000, EPA issued guidance to clarify that the existence of fish or shellfish advisories for a water body constituted impairment under the CWA because the fishable use is not met, even if there were no exceedances of numeric water quality criteria. In addition, EPA asserted that the existence of advisories generally means that the narrative WQS for protecting public health is not met. EPA (2003a) *Guidance for 2004 Assessment, Listing and Reporting Requirements* provides specific criteria for determining impairment:



- The advisory is based on fish and shellfish tissue data;
- A classification below “Approved” (under the National Shellfish Sanitation Program) is based on water column and/or shellfish data;
- The data are collected from the specific segment in question; and
- The risk assessment parameters (e.g., toxicity, risk level, exposure duration, and consumption rate) of the advisory or classification are cumulatively equal to or less protective than those in the state’s water quality standards.

It should be noted, however, that water bodies with a fish consumption advisory do not have to be listed, unless there are water body-specific data. Thus, statewide warnings regarding mercury-contaminated fish based upon a subset of water bodies do not mean that all the state’s water bodies belong on the 303(d) list, and it may be prudent for stakeholders on affected water bodies to object to such blanket listings. However, EPA will allow states to use various monitoring and modeling tools to support extrapolations from a relatively small sampling set. EPA (2002c) guidance states that human health criteria for fish consumption are met as long as the mean concentrations (tissue, water column, etc.) do not exceed the criteria; statistical guidance is also given concerning the number of samples, error rates, etc.

Documentation of listings is presented by states in “Integrated Reports” covering both the requirements of CWA Section 303(d) and Section 305(b), which is an assessment of the state’s waters. When the state releases its draft Integrated Report, permittees should consider how the water body into which they discharge has been assessed. Any category other than “all designated uses are being met” means the state has determined that additional data are needed to make a determination or that the water body is impaired or threatened. Permittees may be able to improve the technical basis of the final decision about the water body by commenting on the assessment methodology or results, or by providing additional data. Once a water body has been listed as impaired, it is difficult for it to be delisted.

### 4.3 EVALUATION AND COMPARISON OF MERCURY TMDL TARGETS

At least 45 states have fish consumption advisories due to mercury and over 1,000 water bodies are listed as being impaired due to mercury. Several methods are generally used in developing mercury TMDLs and each is illustrated in the examples presented in Appendix B and discussed throughout this section. The examples indicate that the TMDL target may be, or include: (1) the concentration in fish tissue, as in the Mermentau-Vermilion-Teche River Basin; (2) the concentration in the water column, as in the Savannah River; or (3) the concentration in suspended sediment, as in San Francisco Bay.

Of the three methods, using a fish tissue concentration as the TMDL target is the most direct measure of the desired endpoint, protection of human health. The fish tissue concentration is influenced by all media to which the fish are exposed (water, sediment, suspended sediment, food) as well as physical, chemical and biological factors influencing that exposure, uptake and depuration. The fish tissue concentration is thus an integrated measure that avoids the assumptions used in calculating water and sediment concentrations. In addition, the target tissue concentration can be established based upon knowledge about fish consumption rates and patterns at the site in question. The disadvantage to using the tissue concentration as a TMDL target is that there is no clear means to apply this target to wastewater dischargers. NPDES permit limits must be expressed in terms of aqueous concentrations or mass loadings. Calculating the appropriate water concentration from the tissue concentration involves the use of numerous assumptions, due to the complexity of mercury cycling and bioaccumulation in aquatic ecosystems. Although the TMDL for the Mermentau and Vermilion-Teche River basins is based on fish tissue concentrations, no conversions were necessary as this TMDL did not provide WLAs for NPDES sources. In addition, this TMDL did not provide an example of the derivation of mercury permit limits or an implementation plan.

The withdrawn Savannah River TMDL is cited by EPA Office of Water as an example of a mercury TMDL. For the Savannah River, the TMDL target was a water column concentration of mercury, derived using site-specific information that would prevent unacceptable bioaccumulation in fish tissue. The use of a water concentration as the TMDL target has the advantage of being compatible with current methods for conducting WLAs and writing NPDES permits. The disadvantage is that the approach is oversimplified and can lead to the implementation of control measures, including unnecessarily restrictive permit limits that are also likely to miss the intended objectives. This simplistic approach assumes a linear relationship between the loadings of total mercury to a water

body and mercury concentrations in fish. However, as discussed in Section 3, evidence indicates that these relationships are much more complex, are influenced by a number of interacting biogeochemical factors, and are highly variable in time and space (AMEC and ENVIRON 2003). It has been argued that load reductions should not be mandated of point or nonpoint sources until additional knowledge about mercury cycling and bioaccumulation allows the establishment of a link between discharges of inorganic mercury and accumulation of methylmercury in fish (AMEC and ENVIRON 2003). Despite these information gaps, states and EPA are likely to continue to develop TMDLs, and permit limits, for mercury.

Finally, the proposed San Francisco Bay TMDL, which was developed by the State of California, established a TMDL using mercury concentrations in suspended sediment as a target. Additional numeric targets were established for human health (a fish tissue concentration target) and for wildlife protection (a bird egg concentration target). The suspended sediment concentration was less subject to short-term fluctuations than water column concentrations and was believed to be a better representation of the amount of mercury in the Bay. Moreover, mercury in San Francisco Bay is not principally from point sources, non-point sources, or atmospheric deposition, but rather is “legacy mercury” associated with sediments from past mining activities.

#### 4.4 ALLOCATION APPROACHES

Determining how to allocate loadings among point and nonpoint sources is the next major part of a TMDL. Several approaches are available including consideration of the relative current contribution of each source. Under this approach, each source would still contribute the same relative percentage of the overall total after the needed reductions in loadings. This was the approach used in the Mermentau Vermilion-Teche and Savannah River TMDLs. Other factors that may be considered are cost-effectiveness, technical and programmatic feasibility, previous experience, past commitments to load reductions, and likelihood of implementation. This last issue is important, because under current EPA guidance, if both point sources and nonpoint sources are contributing to impairment, and the WLAs are based upon assumption of reductions in nonpoint sources, there must be “reasonable assurance” that the nonpoint source controls will achieve the expected reductions. In the Savannah River and Mermentau Vermilion-Teche TMDLs, it was considered acceptable to cite planned controls on air emissions under the Clean Air Act as achieving the necessary nonpoint source load reductions.

EPA’s draft *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* (EPA 2002a, 2004a) offers three approaches to allocation of loadings, depending upon the relative contributions of point source and nonpoint source loadings. First, where point source loadings dominate, the TMDL will specify reductions in these loadings, alone or together with nonpoint source loadings, to attain WQS. An example of such a TMDL for mercury includes water bodies with significant loadings from mining sources. Second, where point source loadings are small, reductions in nonpoint sources are expected to achieve the TMDL. The Savannah River TMDL provides an example. This TMDL determined that a 44% reduction in mercury loadings was needed to reach the water quality target, and that this level of reduction would be expected by 2010 under existing air regulations. Allocations were made for the NPDES discharges, but they were based upon maintaining their current loadings. The third scenario also involves relatively small contributions from point sources, but reductions in nonpoint sources are *not* expected to be sufficient to attain WQS. The mercury TMDL for the Ochlockonee basin in Georgia provides an example. Here, a 76% reduction in loadings is needed, but only 31 – 41% reduction in air loadings is expected. WLAs were developed for facilities identified as significant dischargers of mercury, with the remainder of the allocation divided equally among the remaining point sources.

The San Francisco Bay TMDL used a similar approach to the Savannah River TMDL, in that allocations for NPDES discharges were based upon their current loadings. However, this TMDL considered a broader array of sources of mercury, as well as system losses. Allocations for direct atmospheric deposition and non-urban stormwater runoff, as well as municipal and industrial wastewater, were set at current loadings. To achieve this TMDL, reduced loadings were required from urban stormwater runoff sources (through permitting and pollution prevention), two upstream watersheds (through separate TMDLs), and bed erosion (a natural process).

#### 4.5 IMPLEMENTATION APPROACHES

The approaches used to implement a mercury TMDL will vary depending upon the allocations, as described above. Where there are WLAs to point sources, the traditional method to implement a TMDL is likely to be used (i.e., through the NPDES permit). The implementation of effluent limitations for mercury and other pollutant parameters can be approached through several mechanisms including reasonable potential analysis and development of WQBELs. Where a permittee anticipates mercury limits being incorporated into their permit, they should be



prepared to proactively take steps to understand the concentrations of mercury that are discharged from their facility (and the nature of these sources), the receiving stream characteristics (including sediment and aquatic species), and the policies of permitting and regulating mercury by the permitting authority.

The following subsection provides additional detail on potential approaches and how a permittee can develop supporting data to optimize the permit ultimately issued.

#### 4.5.1 Reasonable Potential

Under the CWA (40 *CFR* 122.44(d)(1)), the permitting authority is required to determine whether a discharger causes, has the *reasonable potential* to cause, or contributes to an exceedance of numeric or narrative water quality criteria. This determination is accomplished through established procedures (that vary from state to state) which account for existing controls on both point and nonpoint sources, variability in chemical concentrations from the permitted effluent, sensitivity of the species to toxicity testing (when evaluating whole effluent toxicity), and dilution of the effluent in the receiving stream where mixing is allowed.

The process for assessing the reasonable potential to cause a water quality violation is one of the main topics covered in water quality standard implementation policy developed by a permitting authority. State permitting authorities may use a variety of methodologies for conducting the reasonable potential evaluation, or may not perform this evaluation at all. When it is done, permitting authorities employ a statistical approach using existing effluent data to predict the upper range of effluent concentrations to compare with a WQS. The permitting authority is allowed under limited circumstances to predict the upper range of effluent concentrations even without actual effluent data, but would have to provide adequate justification for imposing a water quality limit without supporting data.

By its nature, the reasonable potential analysis (RPA) is a conservative exercise conducted by the permitting authority. As permitting authorities seek to implement water quality-based permit limits based on fish tissue concentrations and other new methodologies, the uncertainty of the translators could cause a broadening of the range of discharges regulated. It is incumbent on the permittee to characterize its effluent discharge in a statistically robust manner using data with minimal interferences from sampling and analytical artifacts. This discharge characterization should utilize the sampling and analytical methodologies identified in Section 2 and avoid using elevated detection levels or sampling/analytical artifacts that cause the results to falsely indicate the discharge requires WQBELs. The permittee must also be involved in the processes for developing the RPA (typically during any revision of a state implementation document or in the Continuing Planning Process). It is at that time the permitting authority will identify alternate methodologies for establishing WQBELs and how permitted discharges will be evaluated to determine the RPA.

In the past, RPA assumed mercury was not present in the discharge when the measured mercury concentration was at or below the MDL. With the use of newer, more sensitive analytical methods, it is now possible for the RPA to be conducted at concentrations representative of the water column WQS or even lower. Permittees discharging into water bodies that are listed or likely to be listed as impaired due to mercury should begin to collect data now to properly characterize their discharges.

Permitting authorities will eventually revise the RPA procedure based upon final guidance from EPA on the means to translate from a fish tissue criterion to a water quality criterion. In the meantime, permitting authorities are not likely to establish new procedures for the RPA; rather they will use the existing procedures to make comparisons with the existing water column based water quality criterion or modify the existing RPA procedure to be even more conservative.

#### 4.5.2 NPDES Implementation Procedures

EPA's most recent draft guidance (2004a) offers three different approaches to implement the fish tissue-based criterion in NPDES permits. First, if the state is using a water column concentration, RPA and numeric effluent limits are calculated in the traditional manner (EPA 1991a). This approach assumes that the state has a fish tissue-based water column concentration calculated from a BAF. Second, the state can use a fish tissue value as the water quality standard and then translate this into a water column value for performing RPA and developing WQBELs in the traditional manner. This process also requires use of a BAF (the procedures for developing a BAF were discussed in Section 3).

The third alternative is for the state to adopt a fish tissue-based standard and implement this directly into permits without using a BAF to translate to a water column concentration. EPA (2004a) recommends the third approach

because “it has the advantage of significantly reducing environmental monitoring costs and does not involve developing a site-specific BAF for each waterbody in a State” (p. 75). However, from the permittee’s point of view, this third approach is fraught with problems. This approach rests on the assumption made by EPA that Reasonable Potential exists if two conditions are present: (1) the discharger has mercury present in the effluent at quantifiable levels and (2) fish tissue in the receiving water exceeds the fish tissue water quality criterion. The debatable assumption made by EPA is that the two observations must be linked in a cause and effect manner, e.g., the discharger is at least a contributor to the levels in the fish tissue, even if not necessarily the sole or primary contributor. In addition, EPA’s approach here contradicts the basis of established RPA which holds that the mere presence of a pollutant in an effluent is insufficient to establish reasonable potential. This approach would give the permitting authority flexibility in deciding what types, how much, and what locations are pertinent for fish tissue data collection. The fish tissue data could be acquired by various means, including a requirement for the discharger to monitor fish tissue and water column concentrations. However, it must be emphasized that there is no way to ascertain if the methylmercury in the collected fish is attributable to the discharger.

These three approaches (which exist only in draft form and have not been officially released) are summarized in tabular format, below, along with comments about their potential advantages and disadvantages.

Table 4—Proposed Approaches to Implementation of Fish-Tissue Based Criterion in Permits

Form of fish tissue-based water quality standard	Form of permit limits	BAF needed?	Comments
Water column concentration	Water column concentration	Yes, to develop the water quality standard	Likely to be applied consistently to dischargers statewide; predictable
Fish tissue concentration	Water column concentration	Yes, to develop the permit limit	Could be site-specific for each permittee
Fish tissue concentration	Fish tissue concentration	No	Could require tissue and ambient water column sampling by permittee. Flexible but not predictable. Cannot link tissue concentrations to discharge loads.

Per EPA’s suggested approach (i.e., third option), implementation of the fish tissue-based criterion in permits would begin with effluent monitoring using the appropriate version of EPA Method 1631. If there were quantifiable levels of mercury, the permit would prohibit increased loadings (unless allowed under anti-degradation provisions) and the permittee would also have to develop a mercury minimization plan (if the facility used mercury in any respect or accepted wastewaters that might contain mercury). Even if controls on non-point sources were likely to result in attainment of water quality standards, EPA recommends that a permit contain at least a non-numeric limit prohibiting an increase in mass loadings of mercury and a permit condition for a mercury minimization plan. This is the least of the possible requirements that would be imposed on a permittee. An example of an action that would be part of a mercury minimization plan for a POTW (publicly-owned treatment works) is the development of a public education program. Such a program would seek to minimize the contributions of mercury into the treatment system from dental offices, thermometers, and other sources.

EPA does recommend that the permitting authority consider the contributions from non-point sources of mercury when deriving WQBELs. The Mercury Maps tool (EPA 2001c; 2003d) is cited as a means for identifying sources of mercury in watersheds. However, if the permitting authority does not have sufficient data to assess the contribution of non-point sources, EPA recommends either translating the fish tissue criterion to a water column value and using the traditional approach, or beginning the TMDL development process and determining the WQBELs based on the TMDL.

#### 4.5.3 Development of WQBELs

When the water quality standard for mercury is translated from a fish tissue concentration to a water concentration, it may not necessarily be directly adopted into the permit effluent limit. The permitting authority has some discretion to develop implementation procedures for incorporating water quality considerations into permits. The remainder of this section discusses practices that may be implemented by permitting authorities as part of the development of water quality based effluent limitations, including the use of mixing zones, tiered approaches, and other site-specific criteria.



#### **4.5.3.1 Mixing Zones**

Mixing zones are one method permitting authorities use to establish compliance with water quality criteria. Where the permitting authorities allow for a mixing zone, the permittee does not need to meet applicable water quality criteria at the end of pipe. Instead, ambient concentrations of a given pollutant are allowed to exceed water quality criteria in the immediate effluent discharge area. Some permitting authorities do not allow mixing zones for certain pollutants, or for any pollutants.

Mixing zones are typically limited by size or the percentage of receiving stream flow. In general, an initial zone of dilution is established whereby an acute aquatic criterion must be met to minimize lethal impacts to organisms passing through the zone. At the edge of the mixing zone, the chronic aquatic criterion must be met. The permitting authority can establish the mixing zones through relative flow percentages between the effluent discharge (usually a peak flow) and the receiving stream (usually a critical low flow). The permitting authority can also require that the mixing zone assumptions be validated through receiving stream sampling to ensure the size of the mixing zone is not being exceeded.

#### **4.5.3.2 Tiered approach**

Tiered approaches can be used when permitting authorities have identified receiving stream impairments that must be addressed through point source loading reductions or where water quality standards must be implemented into permits. The most common example of a tiered approach is a permit reopener where additional information becomes available (establishment of a TMDL or identification of a receiving stream impact that must be addressed). Another example is a permit compliance schedule whereby the permittee implements a variety of studies (mass-balance inventory, effluent quality, treatability testing for new wastewater treatment systems, etc.), projects (design/construction of new treatment systems, changes to processes, pollution prevention controls, etc.), or other improvements in order to improve effluent discharge quality. A compliance schedule may also be utilized to better assess/characterize the receiving stream for the development of site-specific criteria. The tiered approach may be appropriately proposed by a permittee where impairments due to pollutants have been identified, but may not be adequately quantified within the receiving stream or within the permittee's discharge. Otherwise the permittee risks the development of a WQBEL that, due to anti-backsliding prohibitions in the CWA, cannot be relaxed upon subsequent gathering of more accurate receiving stream/discharge data.

#### **4.5.3.3 Site-Specific Criteria**

EPA has recognized that the ambient water quality criteria developed for nationwide use may be overprotective or underprotective, depending upon the conditions at a specific site. States are allowed to develop site-specific water quality criteria, and EPA has developed tools for the states to use in this regard. None of these existing tools (the Recalculation Procedure, the Water Effect Ratio Procedure, or the Resident Species Procedure) are applicable for the methylmercury criterion, as they pertain to effects upon aquatic life and not upon human health through bioaccumulation.

States can adopt site-specific modifications to criteria to reflect local conditions and exposure patterns. For methylmercury, in lieu of accepting the 0.3 mg/kg "national" value, the most likely modifications would be to the relative source contribution factor and to the default fish consumption rate (EPA 2002a). Modifications to the default fish consumption rate were used in establishing the target for the mercury TMDLs described in Appendix B.

#### **4.5.4 Other options for implementation**

Options for implementation of a mercury TMDL, other than through traditional permit limits, are available within water bodies and on a regional basis.

##### **4.5.4.1 Within Water Body**

Within a water body, an option for implementation of a mercury TMDL includes a phased approach. A phased TMDL is appropriate where both point and nonpoint source reductions are needed, but the former are dependent upon the latter. This approach is considered "phased" because revisions are needed to accommodate new data, including data on demonstrated reductions. For mercury, a phased TMDL could include monitoring requirements for point source discharges using the newer analytical methods to acquire the data needed for reasonable potential determinations.

Other options include provisions for monitoring, examining pollution prevention programs, evaluating potential technology enhancements to improve plant performance, and conducting studies to evaluate localized impacts and

bioavailability. The San Francisco Bay TMDL included these options in their original TMDL instead of WLAs and WQBELs for permitted dischargers. EPA Region 9, in their review, objected to the lack of WLAs, however, and California did add them to the subsequent Basin Plan, along with a statement that WQBELs would be placed in permits. This contrasts with EPA Region 6 which did not develop WLAs for the Mermentau Vermilion-Teche TMDL. EPA Region 4, in the Savannah River TMDL, offered two options for NPDES permittees. One option presents conservative WLAs, while the other states that WLAs will be developed after mercury minimization methods are implemented. As illustrated, there is currently a great deal of inconsistency in the implementation scenarios for mercury TMDLs, with some EPA regions developing TMDLs that do not contain specific WLAs for permittees, and other EPA regions requiring them.

Finally, EPA has been promoting the concept of watershed-based permitting and trading, which addresses water quality problems on a broader geographical basis, rather than discharge-by-discharge. Activities that may be part of watershed-based permitting range from the synchronization of the permit cycle within a basin to the development of WQBELs on a multi-facility basis. Watershed-based permitting would facilitate water quality trading, which can achieve overall load reductions at lower costs by allowing point and nonpoint sources to trade their allocations. This concept has been applied to pollutants such as phosphorus, nitrogen, and sediment. EPA generally does not support trading of persistent bioaccumulative toxic pollutants (PBTs). Current policy (EPA 2003b) does indicate that EPA would consider supporting a limited number of pilot projects to gauge the potential for trading to reduce PBT loadings in situations where the following conditions are met: the predominant PBT loading does not come from point sources, trading activity does not cause an exceedance of an aquatic or human health criterion, and trading results in a substantial net reduction of the PBT.

#### 4.5.4.2 Regional

Because atmospheric deposition is the major source of mercury in watersheds, and airsheds are larger than watersheds, regional approaches to management of mercury are likely to be necessary to achieve significant reductions in fish tissue mercury levels. Examples of regional approaches that have been suggested include EPA Region 5's draft proposal for a mercury phase-down and the approach proposed by the Quicksilver Caucus (a coalition of state environmental association leaders formed in May 2001).

In EPA Region 5 proposal, a mercury phase-down will address mercury reduction, remediation, and prevention in a variety of media. As part of this program, mercury TMDLs in Region 5 states could be placed at the end of the schedule for TMDL development while these alternative actions occur. If these actions do not result in measurable progress towards achieving WQS, then EPA would expect the TMDLs to be implemented. In July 2004, Region 5 released the *Draft Mercury Pollutant Minimization Program Guidance* (EPA 2004c) which describes how treatment plants, specifically POTWs can identify, reduce, or eliminate mercury loadings according to a plan that would be part of their application for a variance from the WQS for mercury.

Additional action to address mercury as a regional issue is evident in the Quicksilver Caucus proposal. This group feels that developing TMDLs for individual water bodies may not be appropriate, since airborne mercury travels across state borders from regional, national and global sources. As a result, the Quicksilver Caucus was promoting development of a national mercury reduction strategy to supplant the development of mercury TMDLs for individual water bodies.

Unfortunately these regional approaches do not directly or quantitatively link mercury reductions to attainment of water quality standards in a given watershed or water body. These alternatives may require less effort by the states to implement but could be very costly to individual point source dischargers, in some cases with little assurance that standards will be met as a result, and in other cases requiring mercury reductions well below those necessary to attain standards.

Both of these initiatives were mentioned in the 2002 version of EPA's draft implementation guidance, but were deleted from the 2004 version. Despite the apparent lack of progress of these initiatives, states remain concerned about the resources required to perform complex TMDLs, especially where cross-border movement of pollutants is a concern.

## 5 Applicability to Other Metals

Due to the unique properties of mercury in the environment, the issues discussed in this report are not applicable to most other chemicals or metals. EPA has currently only considered development of a tissue-based water quality



criterion for one metal other than mercury, i.e., selenium (69 FR 75541). The revised draft aquatic life criteria document for selenium, containing a tissue-based criterion, was issued for public comment in November 2004 (EPA 2004d). Although selenium does not biomagnify as dramatically as mercury, several instances of fish and wildlife poisoning have been documented at sites affected by selenium from coal-burning power plants and agricultural drainage from seleniferous soils (Lemly 1996).

EPA's *Draft Aquatic Life Water Quality Criteria for Selenium—2004* presents a Final Acute Value (FAV) for selenite in freshwater and saltwater, a freshwater FAV for selenate, and a Final Chronic Value (FCV) for selenium expressed as a whole body tissue concentration. Insufficient data were available to calculate a saltwater FAV for selenate. Consistent with *Guidelines for Deriving Numerical National Water Quality Criteria* (Guidelines) (Stephen, C.E. et al. 1985, EPA 1985), the FAVs and FCVs are calculated based on the results of acute or chronic studies from a minimum number of organisms (i.e., 8 families for acute, 3 taxa for chronic). The FAV is then developed as protective of 95 percent of all taxa evaluated. The FCV may be set based on an acute to chronic ratio or by selecting a value that is protective of a critically important species. In this case, the FCV was based upon a whole body tissue concentration that would be protective of adverse effects in fish.

The freshwater FAV for selenite is based on data for 28 genera for which freshwater mean acute values are available. Of the species evaluated, the four most sensitive genera span a factor of 3.7. The FAV represents the most sensitive 5th percentile genus and was calculated to be 514.9 µg/L. The Criteria Maximum Concentration (CMC) (i.e., the highest concentration that an aquatic community can be briefly exposed to without adverse effects) is calculated to be 257.5 µg/L (EPA 2004d). Data on saltwater exposure to selenite was available for 18 species and therefore, also satisfy the eight family provision outlined in the Guidelines. The four most sensitive genera differ by a factor of 4.7. The saltwater FAV for selenite representing the most sensitive 5th percentile genus was calculated as 253.4 µg/L. The CMC in saltwater was calculated to be 126.7 µg/L (EPA 2004d).

As described in EPA (2004d), a FAV for selenate was developed using a sulfate correction. Numerous studies have shown that selenate toxicity decreases in the presence of sulfate as sulfate competes with selenate for uptake by aquatic organism. Usable data on the acute toxicity of selenate were available for 12 invertebrate species and 11 fish species. Species mean acute values ranged from 593 µg/L for the crustacean, *Daphnia pulicaria* to 1,515,616 µg/L for the leech, *Nepheleopsis obscura*. The four most sensitive genera differ by a factor of 3.0. At a sulfate level of 100 mg/L, the FAV for selenate representing the most sensitive 5th percentile genus was calculated to be 834.4 µg/L. The CMC for selenate is equal to  $e^{(0.5182[\ln \text{ sulfate}] + 3.357)}$  or 417.2 µg/L at a sulfate concentration of 100 mg/L (EPA 2004d).

Similar to mercury, studies have shown that water quality concentrations alone are a poor predictor of selenium uptake and that diet is the most important route of exposure for chronic toxicity to fish (Canton and Van Derveer 1997). As a result, EPA (2004d) developed a tissue-based criterion for selenium. Data indicate that the concentration of selenium in the ovary may be the best predictor of adverse effects; however, due to limited data, whole body tissue concentrations were selected instead (EPA 2004d). Although a tissue based criterion has the advantage of considering the many site-specific conditions that affect selenium uptake and toxicity, it also creates the same implementation issues associated with mercury. As of this publication, EPA has not released any guidance on how to use the tissue-based criterion when determining compliance with water quality standards.

The tissue-based selenium criterion was calculated based on data for an aquatic invertebrate, eight fish species, and a mix of fish species from the family Centrarchidae. These studies were evaluated using either logistic regression to identify the 20 percent response level or best scientific judgment to determine the geometric mean of the no observable adverse effect concentration and the low observable adverse effect concentration. Using these data, EPA (2004d) identified the lowest genus mean chronic value of 9.5 µg Se/g dw whole body based on a study by Coyle et al. (1993) using bluegill. However, these results were lowered to 7.91 µg Se/g dw based on Lemly (1993) that showed adverse effects to bluegill under winter low temperatures (i.e., 4°C). Under 20°C, bluegill exposed in the study by Lemly (1993) only accumulated 5.74 µg Se/g dw. Based on these findings, the FCV for selenium was determined to be 7.91 µg Se/g dw over the winter. However, if the concentration of selenium in whole body fish tissues approaches 5.85 µg Se/g dw during the summer or fall months, EPA recommends additional sampling in the winter to make sure that the FCV of 7.91 µg Se/g dw is not exceeded.

A tissue-based selenium criterion raises many of the same issues as the mercury criterion discussed in this report. Selenium analysis presents significant challenges, due to important differences in toxicity and bioaccumulation potential among selenate, selenite, and seleno-amino acids as well as current limitations in analytical methods. New techniques are currently being developed to better characterize the organic selenium fraction, as this fraction has

been shown to be much more bioavailable than other forms of selenium (EPA 2004d). In addition, the physical distribution of selenium species is influenced by the presence of particulate matter as well as formation of complexes with inorganic and organic colloidal material and humic substances. Selenium associated with particulates or colloidal matter is generally much less bioavailable.

Although bioaccumulation modeling has been undertaken on a site-specific basis for selenium with some success (e.g., Bowie et al. 1996; Schlegel et al. 2004; Brix et al. 2005), the relationship between selenium concentrations in water and tissue is not yet broadly predictable. The factors affecting selenium toxicity and bioaccumulation include sulfate, heavy metals, pH, temperature, and day length (Sappington 2002, EPA 2004d). Several studies have shown that sulfate can reduce selenium uptake to 10 percent of controls and reduce acute toxicity by 90 percent (EPA 2004d). Selenium uptake has also been evaluated in the presence of other heavy metals. Cadmium has consistency shown antagonistic effects to selenium toxicity, while study results for mercury were not in agreement on potential antagonistic/synergistic effects. Finally, pH, temperature, and day length have been shown to have varying effects on selenium uptake. Only acidic pH has been shown to have an effect on uptake of selenite. No effects were seen on other chemical species. As discussed in Lemly (1993), both temperature and day-length appear to influence selenium uptake, with winter simulation (cold temperatures, short days) resulting in greater bioaccumulation.

Given the many site-specific factors that affect selenium uptake, generic BAFs for selenium are expected to entail considerable uncertainty. EPA (2004d) presents a summary of bioconcentration (bioconcentration factors range from 2 to 470 L/kg for fish) and bioaccumulation (BAFs range from 550 to 6,538 for fish) studies for selenium; however, no recommended values are presented. Although development of site-specific BAFs may be appropriate to support the translation from a tissue criterion to a surface water criterion; in contrast to mercury, atmospheric deposition is not a major source of selenium to the aquatic environment. Thus, in water bodies where selenium concentrations in fish tissue exceed an EPA criterion, a greater share of source reduction efforts will fall to industrial effluent dischargers and agricultural operations, as TMDLs are developed and implemented.

In addition to mercury and selenium, the concentrations of other metals and metalloids are sometimes of concern in fish tissue. For instance, fish advisories have been adopted for cadmium, lead, tributyltin, and arsenic (EPA 2004e), although the number of such advisories is quite small in comparison with mercury-related advisories. It appears unlikely that tissue-based criteria would be adopted for these metals, simply because they are not highly bioaccumulative. For instance, arsenic exhibits biodiminution (i.e., lower concentrations at higher trophic levels) (EPA 2003c). Also, arsenic is present in marine fish tissue primarily in a non-toxic organic form; this characteristic may also apply to freshwater fish, although data are currently limited (Donohue and Abernathy 1999; EPA 2003c). Nevertheless, EPA recommends highly restrictive water quality criteria for arsenic for the protection of human health due to fish consumption (EPA 2002e); these criteria are currently being revised. Although tissue-based criteria may not be adopted for arsenic or other metals, bioaccumulation-based water quality criteria are still likely to be over-conservative on a site-specific basis, potentially triggering the need for a site-specific bioaccumulation study.

## 6 Summary and Recommendations

This report summarizes the issues associated with translation of a mercury fish tissue concentration into a water quality criterion. Section 2 presents an overview of the analytical methods available for analyzing total mercury and methylmercury in fish tissue, water, and sediment. Section 3 provides an analysis of the methods and models available to translate the fish tissue concentration into a water quality criterion. Section 4 describes the impacts of the mercury water quality criteria on TMDL development and NPDES permits. Finally, Section 5 discusses the applicability of these issues for other metals. Although the report addresses many topics, it also identified several areas where additional research or study is necessary to fully understand mercury translation in the environment. The following bullets summarize the key findings and recommendations for additional study:

- Validation of methylmercury analytical techniques is necessary to increase the certainty of results.
- Research is needed to improve the national default translators currently proposed by EPA. EPA's data set of BAF,  $f_d$ , and  $K_D$  values should be updated with more recent studies. Additional data would increase the effectiveness of the translator calculation methods by reducing variability and minimizing the uncertainty of the resulting default values.
- National default values are likely to be inaccurate on a site-specific basis, given the very high degree of variability observed in mercury bioaccumulation rates. Models have the potential to account for environmental



factors contributing to this variability, but at present the available models are limited to reservoirs and lakes in a few geographic regions.

- Improvements in national default translators do not decrease the importance of site-specific translators. It is feasible to develop site-specific translators, although the level of sophistication will be driven by costs associated with data collection and testing. As the complexity of the site increases, the perceived need to investigate factors that may contribute to spatial or temporal variation in mercury bioaccumulation will also increase.
- Given the many uncertainties associated with mercury translators, their use should be limited to cases where fish tissue data show exceedance of the tissue-based water quality criterion, and point sources make up a significant contribution to mercury loading in the system. This recommendation is in contrast to the draft EPA guidance, which would allow states to adopt water-based rather than tissue-based mercury criteria for the protection of human health.
- Underlying the use of any type of mercury translator is the premise that mercury levels in fish will respond in a linear manner to reductions in mercury loading.
- It is reasonable to assume that the states, given their lack of resources, will follow the simplest approach, whether or not it is the most scientifically valid. Thus, whole waterbodies or even entire states are likely to be designated impaired and subject to TMDL analyses due to levels of methylmercury in fish, regardless of whether or not site-specific data exist.
- Changes to permit limits are likely to be derived in the absence of a RPA and the accurate consideration of non-point source contributions. To allow permit revisions, many states may default to a state-wide BAFs to allow translation of the fish tissue criterion into a water column value, which can then be implemented in NPDES permits in the traditional manner.
- As the use of EPA Method 1631 becomes more widespread, many dischargers are expected to face extremely low permit limits. At a minimum this will likely entail monitoring for mercury and developing a plan to minimize mercury in discharge waters. In some cases, permittees may be required to monitor ambient waters and local fish tissue.
- The collection of site-specific data affords dischargers opportunities to develop more realistic bioaccumulation scenarios. The cost of this could be shared between groups of dischargers within a waterbody.

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- Bibliography of Selected Recent Studies Available to Update Default Translators for Mercury



## Appendix A—Bibliography of Selected Recent Studies Available to Update Default Translators for Mercury

Reference	Area Studied	Mercury in Fish		Mercury in Water		TSS
		Total	Methyl	Total	Methyl	
Babiarz et al. 2001	Upper Midwest and Southern U.S. streams, wetlands			✓	✓	✓
Baeyens et al. 2003 and refs therein	Belgian estuary and North Sea	✓	✓	✓	✓	
Balogh et al. 2002	Minnesota streams			✓	✓	✓
Balogh et al. 2004	Minnesota streams			✓	✓	✓
Brigham et al. 2002	Minnesota impoundments and lakes			✓	✓	
Brightbill et al. 2004	Delaware River Basin, Mid-Atlantic U.S.	✓		✓	✓	
Brumbaugh et al. 2001; Krabbenhoft 1999	U.S. streams	✓		✓	✓	
Castro et al. 2002	Western Maryland lakes	✓		✓		
Davide et al. 2003	River Po, Italy			✓		✓
Downs et al. 1999	East Anglia, U.K. rivers	✓		✓		
Hope 2003 and refs therein	Willamette River Basin, Oregon	✓		✓	✓	
Kim and Burggraaf 1999	New Zealand lakes		✓	✓	✓	
Le Roux et al. 2001	U.K. estuaries			✓		✓
Lindstrom 2001	Swedish lakes			✓		✓
Mason et al. 2000	Western Maryland streams	✓	✓	✓	✓	
Rolfhus et al. 2003	Lake Superior			✓	✓	✓
Rose et al. 1999	Massachusetts lakes	✓		✓		
Schaefer et al. 2004 and refs therein	New Jersey streams and lakes			✓	✓	
Southworth et al. 2002	Tennessee pond and stream	✓		✓	✓	
St. Louis et al. 2004	Ontario reservoir	✓		✓	✓	
Weech et al. 2004	British Columbia lakes	✓		✓		

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## Appendix B—Example Mercury TMDLs

The examples described below provide different approaches to calculating mercury TMDLs. The Mermentau and Vermilion-Teche River Basin TMDL uses the fish tissue concentration as the TMDL target. This TMDL does not provide WLAs for NPDES sources, and thus does not deal with the issue of having to convert from a fish tissue concentration to a water concentration as would be needed in a permit. The Savannah River TMDL, although since withdrawn, is posted on EPA's web site as an example of a mercury TMDL, indicating that EPA Office of Water favors this approach. For the Savannah River, the TMDL target is a water column concentration of mercury that was derived, using site-specific information, as the concentration that would prevent unacceptable bioaccumulation in fish tissue. The last example is the San Francisco Bay TMDL, which establishes a suspended sediment mercury concentration as a target, in addition to concentrations in fish tissue and bird eggs. This TMDL was developed by the State of California rather than by EPA, and was criticized by EPA in a number of areas.

A brief description of all of the components of each TMDL is provided; however, a critical evaluation of each is beyond the scope of this report.

### MERCURY TMDL FOR MERMENTAU AND VERMILION-TECHE RIVER BASINS

This TMDL was developed by EPA Region 6 for subsegments within the Mermentau and Vermilion-Teche River basins in Louisiana (EPA 2001a).

*TMDL Triggers:* The water bodies were listed due to excessive levels of mercury in fish tissue, and fish consumption advisories issued by the State of Louisiana. Louisiana also has numeric water quality standards for mercury for the protection of aquatic life.

*Approach:* Fish tissue concentration was used as an indicator of loading. The TMDL was developed for the watershed as a whole and was not spatially explicit.

*Source assessment:* Air emissions data for facilities located within 100 km around the watershed were used to evaluate nonpoint sources. Wet and dry deposition was estimated from the National Mercury Deposition Program data. Existing point source loadings (wastewater discharges) were calculated using discharge flow data and an assumed concentration of 15 ng/L mercury for all discharges. (This concentration was based upon data collected in Arkansas using sensitive analytical techniques). Point source contributions represented only 0.6% – 1.5% of the total loadings.

*Numeric targets:* Louisiana does not have a numeric standard for mercury to address human health effects from mercury bioaccumulation. Instead, the TMDL uses a target concentration of 0.4 ppm total mercury (wet weight) in fish, calculated as the concentration that triggers the state's advisories (0.5 ppm) multiplied by a safety factor (20%). This concentration was supported by Region 6 because it is similar to a value calculated using EPA's human health methodology (EPA 2000c) with the standard assumptions and a state-specific fish consumption rate (0.35 ppm), as well as being similar to EPA's methylmercury tissue criterion of 0.3 ppm. A numeric target for water column concentrations was not determined.

*Linkage:* A direct linear relationship between atmospheric loading and fish tissue concentration was assumed, based upon EPA's modeling results (EPA 1997). To establish the degree of mercury reduction needed in key fish species, the "worst case" body burden was divided by the target (safe) tissue concentration level. The worst case average tissue concentration was found in bowfin in one of the watershed segments. The ratio of this concentration (1.191 ppm) to the target concentration (0.4 ppm) indicates that a 67% reduction in loading is needed.

*Allocations and Implementation:* Mercury reductions are expected to occur in a phased fashion through regulatory controls under the Clean Air Act. These reductions are expected to result in attainment of the TMDL target. Specific load allocations for nonpoint sources and WLAs for point sources were not presented in the TMDL, and an implementation plan was not included. Wet deposition rate and fish tissue body burdens will be monitored to indicate the effectiveness of the TMDL. When written, the implementation plan would identify point sources with a reasonable potential for exceeding water quality standards for mercury and will require monitoring of those discharges. Mercury loading from those facilities would be controlled through permit limits or through implementation of a mercury minimization plan. Details on how this would be accomplished are not provided.

## MIDDLE AND LOWER SAVANNAH RIVER MERCURY TMDL

The mercury TMDL for the Middle and Lower Savannah River was completed by EPA Region 4 in February 2001, at the request of the State of Georgia, in compliance with a court-ordered deadline (EPA 2001b). Subsequently, Georgia adopted EPA's new methylmercury criterion, under which the Savannah River is no longer listed as impaired. However this TMDL remains on EPA's TMDL web site as an example mercury TMDL.

*TMDL Triggers:* Several sections of the Savannah River were placed on Georgia's 303(d) list because mercury in certain species of fish exceeded fish consumption guidelines established by the Georgia Department of Natural Resources. Georgia has a numeric water quality standard for the protection of aquatic life (12 ng/L), but EPA determined that this was not protective of public health. The applicable water quality standard under which the TMDL was developed was the state's narrative standard for toxic substances.

*Approach:* Current loadings were evaluated using modeling techniques and available data on mercury in the water column, sediment, soil, and fish tissue. A Watershed Characterization System (WCS) model developed by EPA Region 4 was used to simulate precipitation-driven runoff and sediment delivery, based upon data on wet and dry deposition rates of mercury. The Water Quality Analysis Simulation Program (WASP5) water quality model, a general dynamic mass balance framework, was used to model mercury fate and transport in the system. The average annual flow and average annual loading were used as the critical conditions. The calculated allowable load that would not exceed the applicable water quality standard (water column concentration) was determined to identify needed reductions in loadings.

*Source assessment:* The assessment indicated that 99% of the loading is from atmospheric sources within a 100-km boundary around the watershed, which were considered to be nonpoint sources, and the remaining 1% considered to be from point source wastewater discharges. The TMDL states: "Because of the pervasive nature of mercury, and its presence in rainwater, it is assumed that all NPDES facilities discharge some mercury to the river." Most of these facilities have not detected mercury (due to the lack of sensitivity of the methods used), have not demonstrated "reasonable potential", and do not currently have permit limits for mercury. However, during TMDL development, limited sampling was conducted using EPA method 1631, Revision B, which confirmed that half of the 22 facilities sampled were discharging mercury at concentrations above 2.8 ng/L. Based upon this one-time sampling event, it was estimated that point sources contributed approximately 1% of the current total load of mercury to the Savannah River.

*Numeric targets:* A numeric target for human health protection was derived using EPA's human health methodology (EPA 2000c), resulting in a fish tissue residue value of 0.4 mg/kg determined to be protective of the general population. To translate this value to a water column value, the recommended national values in EPA's Human Health Methodology were used for the fish consumption rate, average lifetime and mercury reference dose. Site-specific data were used for the bioaccumulation factor (4,000,000) and for the fraction of total mercury as methylmercury (0.0353). The BAF was selected from the central tendency of the measured data for a fish 315 mm in length. Only fish from Trophic Level 4 were used, conservatively assuming consumption of only largemouth bass. The methylmercury fraction represents the median of data from across the watershed. The site-specific data were collected during a one-time sampling event. Using this approach, EPA interpreted Georgia's water quality standard for total mercury as 2.8 ng/L.

*Linkage:* The current loading conditions and the modeling approach explained previously were used to develop a relationship between mercury loading and water column mercury concentrations. This relationship was stated to be linear and was used to develop the total load. Using the highest water column concentration of mercury observed (5 ng/L) and the current load (58.8 kg/year), it was calculated that the load needed to be reduced to 32.8 kg/year to attain a water column concentration of 2.8 ng/L.

*Allocations and Implementation:* Loadings need to be reduced by 44% to meet the desired water column concentration. Allocation percentages were set equal to source contributions, e.g., 99% to atmospheric sources (32.5 kg/year) and 1% to wastewater discharges (0.3 kg/year). Atmospheric loadings are expected to be reduced due to implementation of Clean Air Act Requirements. For wastewater discharges, only one permitted facility had a limit for mercury; 24 facilities were identified with flow greater than 1 million gallons per day (MGD) or as "major industrial facilities;" and 4 additional facilities were identified based upon data collected indicating they may be discharging mercury above 2.8 ng/L. The TMDL did not provide WLAs for 50 other NPDES permitted facilities because their flow was less than 1 MGD or they were considered "minor industrial" facilities. As the new more



sensitive analytical method is implemented in the NPDES permit program, monitoring will indicate whether these smaller facilities are contributing mercury.

In this TMDL, EPA determined that “as a matter of policy, NPDES point sources known to discharge mercury at levels above the amount present in their source water should reduce their loadings of mercury using appropriate, cost-effective mercury minimization methods.” For the 29 permitted facilities, the TMDL provided WLAs in two different forms, and authorized the permitting authority to apply either form. Option A is to apply the interpreted WQS (2.8 ng/L) to the discharger’s effluent at the outfall point. This is extremely conservative, as the sum of the WLAs determined in this manner for the 29 dischargers is 0.001 kg/year, significantly less than the cumulative WLA needed (0.3 kg/year) to meet the TMDL. Under Option B, the individual WLAs are determined after implementation of mercury minimization methods. This option requires: revision of existing NPDES permits to include WQBELs for mercury, along with requirements to characterize the effluents using the most current version of EPA Method 1631; requirements to develop a mercury minimization plan if the data shows that effluent mercury is present at concentrations greater than influent or source water and the effluent concentration exceeds 2.8 ng/L; and a requirement to implement “cost-effective mercury minimization methods”, if indicated.

### **SAN FRANCISCO BAY MERCURY TMDL**

A report on mercury in San Francisco Bay was prepared by the California Regional Water Quality Control Board (CalWQCB), San Francisco Bay Region (Johnson and Looker 2003). This report serves as the basis for a Basin Plan Amendment, which, if adopted, will establish a TMDL for mercury in the Bay. The Basin Plan Amendment was released in April 2004 (San Francisco Bay Regional Water Quality Control Board, 2004a) and revised in September 2004 (ibid, 2004b). The proposed TMDL is based upon a target mercury concentration in suspended sediment. This was preferable to a water column mercury target because sediment and suspended sediment mercury concentrations are expected to relate better to the amount of mercury in the Bay and are less subject to short-term fluctuations. Moreover, the principal source of mercury in San Francisco Bay is not point sources, non-point sources, or atmospheric deposition, but rather is “legacy mercury” associated with sediments from past mining activities that are coming from upstream watersheds.

*TMDL triggers:* Elevated mercury levels in fish from San Francisco Bay led the California Office of Environmental Health Hazard Assessment to issue a fish consumption advisory for sport fishing in San Francisco Bay. In addition, high mercury concentrations have been found in the eggs of piscivorous birds, which impairs the beneficial use of the Bay as wildlife habitat and for protection of rare and endangered species. Three water quality objectives apply to San Francisco Bay: a water concentration of 0.025 µg/L total mercury (4-day average) in a particular section of the Bay; a bay-wide concentration of total mercury of 0.051 µg/L; and a narrative water quality objective limiting bioaccumulative substances where controllable factors are responsible.

*Approach:* Insufficient data were available to characterize the complex fate and transport processes for mercury in the Bay. Thus, a simple mass balance model was used, in which the Bay was treated as a single compartment with the sediment component (but not the mercury sources and losses) at steady state.

*Sources and Losses:* The sources of mercury to San Francisco Bay were identified as bed erosion (largest source), two upstream watersheds, urban and non-urban stormwater runoff, direct atmospheric deposition on the Bay, and wastewater discharges. Losses occur through dredging, evaporation, and sediment transport to the ocean.

*Numeric targets:* The numeric targets were set to a mercury concentration of 0.2 ppm in fish tissue and 0.5 ppm in bird eggs, representing a 40% and 50% reduction in current levels, respectively. The fish tissue target was based upon EPA’s national methylmercury criterion, adjusted to reflect local fish consumption patterns. The target will be evaluated by tracking the mercury concentration in striped bass. To achieve these targets and attain water quality standards, the concentration of mercury in suspended sediment must be reduced to a median target concentration of 0.2 ppm. (A water column target concentration was not established).

*Linkage:* Because most mercury in the Bay is bound to sediment, reductions in suspended sediment concentrations are expected to result in proportional reductions in tissue concentrations and attainment of WQS. The relationship between water column, sediment, and fish tissue mercury levels is assumed to be linear, in the absence of sufficient information to determine otherwise. To meet the targets, the amount of mercury in the Bay needs to be reduced by about 50%.

*Allocations and Implementation:* The proposed allocations call for substantial reductions in the loads from bed erosion, urban stormwater runoff, and two upstream watersheds. Separate TMDLs will be completed for the

upstream watersheds, one of which has legacy chemicals from mining activities. Mercury loads will be reduced from urban stormwater sources through NPDES permits and pollution prevention programs. Bed erosion is a natural, uncontrollable process that will continue and will result in an eventual decrease in the sediment mercury concentration. Allocations for other sources (direct atmospheric deposition, non-urban stormwater runoff, and municipal and industrial wastewater) were set at current loadings. It is projected that, under the TMDL, the sediment mercury concentration would reach the target level after approximately 120 years.

Adaptive implementation is proposed for this TMDL, in which new information will be reviewed and incorporated every five years. Load allocations were set as a group mass limit for municipal wastewater dischargers and for the industrial wastewater dischargers. Individual wasteload allocations were also established. Each discharger will be assigned performance-based effluent triggers for the monthly average and daily maximum in its effluent. All NPDES permits will contain provisions that specify required actions if these concentration-based trigger values are exceeded. For industrial dischargers, the triggers are: daily maximum 0.062 µg/L total mercury (derived from the 99th percentile concentration of effluent data collected over a specified period) and a monthly average of 0.037 µg/L total mercury (derived from the 95th percentile concentration of effluent data collected over a specified period). Similar triggers were established for municipal dischargers. If the triggers are exceeded, the facility is to evaluate the cause of the exceedance, examine existing pollution prevention programs and possible improvements, evaluate potential technology enhancements to improve plant performance, and evaluate the existing monitoring program. In addition, the TMDL proposed that industrial dischargers (as well as other stakeholders) be required to undertake studies to evaluate localized impacts and bioavailability.

The TMDL also proposed that the following requirements be incorporated into the watershed NPDES permit for municipal dischargers and the individual NPDES permits for industrial wastewater dischargers in San Francisco Bay:

- Develop and implement effective programs to control mercury sources and loadings;
- Comply with WQBELs, to be elaborated through the permit, that are consistent with the mercury wasteload allocation;
- Cause, or cause to be conducted studies aimed at better understanding the bioavailability of mercury sources, and mercury fate, transport and biological uptake in the Bay;
- Cause, or cause to be conducted studies on the potential for localized effects in the vicinity of discharges; and
- Prepare an annual report that documents mercury load data and source control/pollution prevention activities.

In addition, the TMDL proposed that petroleum refineries work with the Water Board to conduct an evaluation of the environmental fate of mercury in crude oil.

This TMDL has not been acted upon (either approved or disapproved) by EPA Region 9 as of this writing

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