

Association of Metropolitan Sewerage Agencies

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Gary J. Brower, Esq. Attn. DEP Docket Number 28-02-10/347 Office of Legal Affairs New Jersey Department of Environmental Protection P.O. Box 402 Trenton, NJ 08625-0402

Re: Proposed Amendments to Surface Water Quality Standards at N.J.A.C. 7:98 to Add Wildlife Criteria for DDT, Mercury and PCBs, New Jersey Register (November 18, 2002 at 34 N.J.R. 3889(a)) and Notice of Extension of Public Comment (January 9, 2003)

Dear Mr. Brower:

The Association of Metropolitan Sewerage Agencies (AMSA) is pleased to comment on the New Jersey Department of Environmental Protection's (Department or DEP's) proposal to amend the State's water quality standards to include wildlife criteria for mercury. AMSA represents nearly 300 publicly owned treatment works (POTWs) nationwide, including 18 members in New Jersey, who every day treat over 18 billion gallons of wastewater and provide sewer service to more than 180 million Americans. AMSA members are very interested in the development of water quality standards for mercury for the protection of wildlife and human health, and have been actively involved with the development and review of standards for the Great Lakes region, research related to wildlife criteria, and the development of national standards and guidance for the methylmercury human health criteria.

The proposed New Jersey wildlife values are based on the wildlife criteria methodology that was developed in the Great Lakes Water Quality Initiative (GLWQI) and that was, for mercury, subsequently applied with modifications in an ecological risk assessment for EPA's Mercury Study Report to Congress (MSRC). The GLWQI methodology was based on the water quality criteria derivation methodology previously developed by EPA for protection of human health for non-

carcinogens. Similarly, it is an approach that relies on test doses (i.e., NOAELs, LOAELs) from toxicological studies and on uncertainty factors intended to account for the unknowns associated with extrapolations from those test doses.

### **Uncertainty Factors**

One of the uncertainty factors applied in the proposed New Jersey derivation is the interspecies uncertainty factor (UF<sub>A</sub>). For mercury, the proposed derivation adopts the MSRC value of one rather than the GLWQI value of three. We agree with the MSRC justification that a UF<sub>A</sub> greater than one is unnecessary because "a review of the literature suggests that piscivorous birds possess a greater capability to detoxify methylmercury than do non-piscivorous birds [e.g., the mallard duck]." Attached to these comments are examples from published literature that provide further support for this conclusion.

However, a review of this literature must also lead one to question the suitability of the mallard duck as a toxicological surrogate for the bald eagle, the osprey and the peregrine falcon, all of which are much higher in the food chain. A capability to detoxify methylmercury is an evolutionary adaptation by upper trophic level species in response to this naturally occurring bioaccumulative toxicant. On the other hand, the mallard duck, having no need for such an adaptation, could not have evolved a methylmercury detoxification capability. It is therefore unreasonable to assume that it shares with the predatory species a comparable level of toxicological sensitivity to mercury, and we oppose the use of mallard duck data to protect eagles, ospreys, and falcons.

Another uncertainty factor applied in the proposed New Jersey derivation is the LOAEL-to-NOAEL uncertainty factor (UF<sub>L</sub>). For mercury, the proposed derivation adopts the MSRC UF<sub>L</sub> value of three rather than the GLWQI UF<sub>L</sub> value of two. Yet the only apparent justification provided for this choice is the MSRC observation that, "given the substantial uncertainties in all the values used to calculate the (wildlife criteria) for mercury exposure, neither two nor three can be considered the only correct value."

The GLWQI selection of two for its  $UF_L$  value was consistent with its statement that "severity of effects is not to be considered when determining the value of  $UF_L$ ... since a more narrowly defined set of frank effects (e.g., growth, reproductive and developmental impairment) is used in the context of protecting populations" (EPA-820-B-95-009, p. 28). An emphasis on protecting wildlife *populations* is also indicated in the New Jersey document's background section where it states that "minimizing incidental take required the derivation of criteria using population impairment endpoints." We therefore contend that, as in the GLWQI, using two as the UF<sub>L</sub> value for mercury would be an appropriate choice, and increasing the UF<sub>L</sub> value to three lacks sufficient justification and scientific evidence where the goal is protection at the population level.

## Other Derivation Assumptions

The assumed peregrine falcon diet is another component of the proposed New Jersey derivation that lacks adequate scientific justification. The fraction of the peregrine falcon prey that is composed of piscivorous birds is critical, because currently the peregrine falcon, more than any other wildlife species, drives the stringency of these criteria. This might not be the case if a significantly lower fraction is assumed for piscivorous prey. Yet, the document concedes, "no definitive data could be found indicating

what percent of all New Jersey peregrine falcons' diet is composed of piscivorous birds." Considering the magnitude of the effect of this assumption on the derived criteria, more definitive data is clearly called for before proceeding with adoption and implementation.

Contrary to its stated intent to "derive New Jersey-specific criteria", the proposed New Jersey derivation adopts single-value dissolved methylmercury bioaccumulation factors (BAFs) calculated for the MSRC from North American and European data. No bioaccumulation data specific to New Jersey locations are used. This problem is further compounded by the adjustment of these BAFs to represent the concentration of total mercury in unfiltered water. MSRC methylmercury concentrations are averaged to represent what is acknowledged to be a "worldwide" methylmercury percentage. There is no consideration whatsoever of any New Jersey-specific data for pH, dissolved organic carbon (DOC), or methylmercury concentrations, although all of these factors are actually much better predictors of mercury bioaccumulation than total mercury in water. In fact, the concentration of total mercury in water has been determined to have an *insignificant* influence on mercury bioaccumulation, and "use of total mercury concentration in surface water, as an indicator of potential mercury accumulation risk to fish, piscivorous wildlife and humans, is invalid and inappropriate" (Teed et al., Assessment of Existing Methods and Data Development for Revising Water Quality Criteria for Protection of Wildlife for Mercury, presented at WEFTEC 2002). Additional information on the uncertainties involved with translating water column or sediment concentrations to fish tissue concentrations based upon BAFs can be found in the attached report entitled "Implementation of EPA's Methylmercury Criterion for Fish Tissue" (AMEC Earth & Environmental and ENVIRON, January 24, 2003).

Despite the claim that bald eagle, osprey and peregrine falcon "populations have been affected by exposure to DDTr, PCBs, and mercury," the proposal presents no evidence whatsoever of wildlife populations being adversely affected by mercury bioaccumulation at current levels. On the contrary, the document provides information describing recent successes in New Jersey populations of each of the avian wildlife species to be protected. This is the case despite the fact that the current mercury levels in New Jersey waters are almost certainly well above the proposed criteria. Analyses of mercury in waters elsewhere have demonstrated that exceedance of the proposed criterion of 0.53 ng/L is widespread. At least for mercury, the document is incorrect in stating that "the contaminant concentrations proposed would most likely be below any commonly used analytical detection limits currently available." EPA Method 1631, "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" with a method detection limit of 0.2 ng/L, has been in use for more than a decade and was approved by the EPA in 1999 for the analysis of total mercury in wastewater. Application of this method in the analysis of New Jersey waters could provide a "reality check" that would call into question the need for criteria values as stringent as those proposed to protect New Jersey wildlife.

# Attainability and Cost

AMSA believes that DEP has not completely met its obligations pursuant to the New Jersey Administrative Procedures Act. NJSA 52:14B-4(a)(2) requires DEP to:

"Prepare for public distribution at the time the notice appears in the Register a statement setting forth a summary of the proposed rule, a clear and concise explanation of the purpose and effect of

the rule, the specific legal authority under which its adoption is authorized, a description of the expected socio-economic impact of the rule, a regulatory flexibility analysis, or the statement of finding that a regulatory flexibility analysis is not required, as provided in section 4 of P.L.1986, c.169 (C.52:14B-19), a jobs impact statement which shall include an assessment of the number of jobs to be generated or lost if the proposed rule takes effect, and an agriculture industry impact statement as provided in section 7 of P.L.1998, c.48 (C.4:1C-10.3)."

On pages 45-46 of the notice, DEP responds by stating:

"As discussed in the Economic Impact Statement, the imposition of requirements based on the SWQS is waterbody and facility specific. Failure to implement the proposed amendments could result in lost employment opportunities in businesses and industries that are water quality depended, such as tourism and fishing. The implementation of the SWQS through the NJNPDES permitting and other NJDEP programs will continue to result in job opportunities in analytical and environmental consulting services to assess permit compliance and evaluate and design the most cost effective abatement measures to achieve permit compliance. Should such abatement involve new capital improvements, job opportunities related to construction contracting services and operation and maintenance of these improvements would be created."

DEP's response does not completely address the socio-economic impact of the rule as it does not consider if the proposed mercury wildlife standard is attainable by dischargers in the state, and if not what the proposed costs for compliance may be.

As a case in point, consider the wildlife criterion for mercury of 1.3 ng/L adopted as part of EPA's promulgation of the final Water Quality Guidance for the Great Lakes in May 1995. At the time the criteria were adopted, EPA falsely assumed that elimination/minimization of mercury from industrial sources such as dental facilities and hospitals would result in "zero discharge" or at least enable POTWs to meet the criteria. This conclusion was based on a limited sampling study conducted by EPA in 1994 at nine POTWs (a single grab sample was collected from each plant).<sup>1</sup> These data showed that total mercury was detected in five of the nine samples at levels ranging from 3 to 36 ng/L, and was not detected at four of the plants.<sup>2</sup> In 1999, AMSA collected mercury data from 23 POTWs throughout the country that had used sensitive sampling and analytical methods. These data showed that none of the plants had mercury concentrations less than detection in 397 sample events.<sup>3</sup> In 2000, AMSA performed additional sampling and analysis at two of the four POTWs from EPA's study that had non-detectable levels of mercury in their wastewater. Another one of these four POTWs performed its own sampling and analysis at that time. Based on ten samples from each plant, the average concentration of all the samples was just above

<sup>&</sup>lt;sup>1</sup> U.S. Environmental Protection Agency, <u>An Analytical Survey of Nine POTWs from the Great Lakes Basin</u> (Draft Report, December 15, 1994), p. 1.

<sup>&</sup>lt;sup>2</sup> U.S. Environmental Protection Agency, <u>An Analytical Survey of Nine POTWs from the Great Lakes Basin</u> (Draft Report, December 15, 1994), p. 1.

<sup>&</sup>lt;sup>3</sup> May 20, 1999 Letter to Tudor Davies, EPA Office of Science and Technology.

2 ng/L, but well above the Great Lakes wildlife criterion and about four times higher than the proposed New Jersey criterion.<sup>4</sup>

With regard to the feasibility of source control to reduce mercury levels in wastewater to comply with stringent wildlife criteria, AMSA conducted a study under a cooperative agreement with EPA ("Mercury Source Control and Pollution Prevention Program Evaluation Final Report," March 2002, Larry Walker Associates, Davis, CA). The goals of the project were to evaluate the effectiveness of POTW pollution prevention (P2) programs at reducing mercury loadings to POTWs and to determine if these reductions could enable POTWs to comply with new, lower effluent limits for mercury. The project clearly demonstrated that mercury source control and P2 programs have the potential to achieve measurable reductions in POTW influent and to have positive impacts with respect to reducing other environmental releases of mercury. However, while mercury source control and P2 will play a key role in efforts to reduce mercury loadings to POTWs, the project demonstrated that the extent to which they will enable POTWs to meet increasingly stringent effluent limits appears limited. A copy of this report is attached.

In addition to not determining the attainability of the proposed criterion, DEP has failed to determine the costs of complying with the criterion via NPDES permits and/or TMDLs. These costs can be exorbitant as evidenced by studies undertaken by the Ohio EPA in cooperation with stakeholders from municipalities, industries and environmental organizations with regard to the GLWQI mercury wildlife criterion of 1.3 ng/L. This consortium developed a statewide variance option for mercury in light of concerns over the inability of NPDES permit-holders to comply with the wildlife criterion. As part of this effort, Foster Wheeler Environmental Corporation and DRI/McGraw-Hill conducted a statewide macro-economic study.<sup>5</sup> The results of the study showed that, in lieu of regulatory options including the mercury variance, the total annualized cost to implement the Great Lakes Water Quality Guidance in Ohio would be more than \$1 billion dollars. In addition, the study showed that a treatment technology did not exist to remove mercury to achieve the GLWQI wildlife criterion of 1.3 ng/L. Vendors would only guarantee removal to 100 ng/L using a system comprised of activated sludge, chemical precipitation, ion exchange and reverse osmosis.<sup>6</sup> The estimated removal cost was between \$10 million and \$100 million per pound (\$2 to \$5 per gallon of effluent stream).

Given that NJDEP's proposed mercury criterion of 0.53 ng/L is more than 50% lower than the Ohio criteria, similar or greater costs would be likely and should be considered as part of this rulemaking effort.

<sup>&</sup>lt;sup>4</sup> May 5, 2000 Letter to Tudor Davies, EPA Office of Science and Technology.

<sup>&</sup>lt;sup>5</sup> Reash, Robin J., Loeffelman, Paul H., Hollback, John E., Tiell, Jennifer and Martin, Gary. "Now You Can Choose: Treat Mercury in Water at \$10 Million Per Pound or Take Ohio EPA's Statewide Variance with Pollution Minimization." *Environmental Regulation and Permitting*, Spring 1998, pgs 29 - 38.

<sup>&</sup>lt;sup>6</sup> This work was done prior to promulgation of an approved mercury method capable of detecting mercury below 1 ng/L.

The cost estimates from the Ohio variance are not an anomaly. The costs of applying microfiltration/reverse osmosis technologies have been evaluated by the County Sanitation Districts of Los Angeles County (Sanitation Districts). The Sanitation Districts are a confederation of independent special districts serving about 5.4 million people in Los Angeles County. The Sanitation Districts' service area covers approximately 800 square miles and encompasses 78 cities and unincorporated territory within the County. The agency operates 11 wastewater treatment plants that convey and treat approximately 530 million gallons per day (mgd), 190 mgd of which are available for reuse in the dry Southern California climate. As part of recent permit compliance evaluations, the Sanitation Districts asked the engineering consulting firm of Montgomery, Watson, Harza to evaluate the costs of applying microfiltration/reverse osmosis treatment to five of the Sanitation Districts' tertiary water reclamation plants. This information was utilized to calculate what the cost of mercury removal would be if this treatment technology were applied (note: this does not consider if the effluent would comply with mercury levels below 1 ng/L). The estimated cost (flow weighted average) was determined to be \$21.9 million per pound of mercury removed (this includes a brine line and ocean outfall to dispose of the reject from the membranes). The cost without a brine line and outfall would be \$19.1 million per pound of mercury removed. In locations that have no access to ocean disposal or if concentrated brines are not allowed for ocean disposal, the costs would be significantly higher inasmuch as it would require some form of distillation to treat the brine to a residue for disposal as a hazardous waste.

## Conclusion

In conclusion, AMSA requests that DEP reconsider its proposal to promulgate wildlife criteria until it has had the opportunity to consider the additional scientific evidence presented above and the time to:

- Derive criteria that:
  - Are based on toxicological data for the wildlife species to be protected and not for nonpiscivorous species or species occupying a lower trophic level;
  - Apply uncertainty factors no greater than is necessary to provide protection at the population level;
  - Apply dietary and other exposure assumptions that are based on definitive, geographicallyappropriate data;
  - Fully take into account the many site-specific variables in water chemistry, food web structure, and watershed characteristics that influence bioaccumulation. In lieu of the ability to do this, the DEP should abandon the methodology that applies BAFs to derive criteria for the total pollutant in the water column. The DEP should instead consider an approach that relies upon criteria representing the pollutant concentrations in fish tissue that would be protective of wildlife species.
- Conduct an analysis of the ability to attain the criteria in New Jersey waters and in regulated discharges to those waters; and
- Conduct an analysis of the costs to regulated dischargers associated with compliance with effluent limitations to be based upon the criteria.

AMSA appreciates the opportunity to provide comments on this matter. If you have any questions, please contact me at 202-833-9106 or *chornback@amsa-cleanwater.org*.

Sincerely,

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Christopher Hornback Director, Regulatory Affairs

ATTACHMENTS

Following are quotations from literature cited in the Mercury Study Report to Congress (1997) which support the EPA's decision to not use an interspecies uncertainty factor greater than 1 in the Report's wildlife criteria derivation:

# Norheim, G. and A. Frøslie (1978). The degree of methylation and organ distribution of mercury in some birds of prey in Norway. *Acta. Pharmacol. Toxicol.* 43:196-204:

- "It cannot be concluded from the pathological examinations (Holt *et al.* 1979) that the birds with the highest mercury levels suffered from a real mercurialism, and probably the excretion of inorganic mercury has been in balance with the biotransformation and the methyl mercury intake itself."
- "The demethylation of methyl mercury is, therefore, a significant detoxification route for methyl mercury in birds of prey, so that they, in spite of their high exposure due to their position as the final link in the food chain, tolerate methyl mercury better than has previously been believed."

# Fimreite, N. (1974). Mercury contamination of aquatic birds in northwestern Ontario. *J. Wildl. Manage.* 38:120-131:

- "It is interesting to compare mergansers with mallards. Although the former contained the highest total mercury levels in liver (10.7 versus 5.46 ppm), the methyl mercury levels, in contrast, are significantly higher in mallard both with respect to liver and muscle values."
- "It is well known that vegetarians contain a rich microflora taking part in the digestion process. The capability of such microorganisms . . . to convert inorganic mercury to the methyl form has been proved (Wood 1972). It is therefore reasonable to believe that such a process takes place during the digestion process and accounts for the high methyl mercury fraction in the [stomach content vegetable and invertebrate] material analyzed in this study. This may also explain the corresponding high methyl mercury levels in body tissues of the ducks from which the stomach contents were taken. Such a process may be of less significance in fish-eating birds lacking the rich microflora."
- "... [T]he bulk of the mercury in a typical fisheater like common merganser did not occur in a methyl form which, in this case, averaged only 12.3 percent of the total mercury content. The considerably higher methyl mercury fractions in surface-feeding ducks (mallards and pintails) [both about 90 percent vegetarians] and in common goldeneye [chiefly an invertebrate feeder] indicate an interspecific variance which is not fully understood but may be related to differences in the secretion mechanism or in the intestinal microflora possibly taking part in an in vivo methylation of inorganic mercury. In any event, these findings strongly imply that, as least as far as ducks are concerned, the total mercury content is no satisfactory indicator of the levels of methyl mercury which

is recognized as this heavy metal's most dangerous form."

# Jernelöv, A., A. H. Johansson, L. Sörenson and A. Svenson (1976). Methyl mercury degradation in mink. *Toxicol.* 315-321:

- "The differences in the methyl/total mercury ratio between marine and terrestrial animals might have some evolutionary explanation. Mammals living in areas contaminated with methyl mercury or eating contaminated food for long periods might have become adapted to resist and even to decompose methyl mercury in the way that some microorganisms do."
- "... [C]ats contained more methyl mercury in the brain than did mink after essentially identical feeding with methyl mercury. The cats also showed symptoms of severe poisoning. The mink showed no obvious symptoms of poisoning and their behavior was unchanged throughout the experimental period."
- "... [T]he amounts [of inorganic mercury] obtained [in the mink] are higher than might be explained simply by accumulation from food contaminated with inorganic mercury as well as methyl mercury. The only plausible explanation is that demethylation of methyl mercury has occurred in the mink."
- "Mink seem to resist methyl mercury better than the cats fed with methyl mercury-contaminated fish, as can be seen from the distribution in the brain and a comparison of the accumulation of inorganic mercury in liver and kidney. Seals and other marine mammals, exposed to methyl mercury through their food, contain however higher proportions of mercury as inorganic mercury in liver tissue. Whether this is due to longer time of exposure to methyl mercury or a more efficient system for conversion is not yet determined. The time course of accumulation of inorganic mercury in mink indicates, however, a less efficient [methyl mercury] degrading capacity [than in marine mammals]."

# Wren, C.D., P.M. Stokes and K. L. Fisher (1986). Mercury levels in Ontario mink and otter relative to food levels and environmental acidification. *Can. J. Zool.* 64:2854-2859:

- "The low proportion of organic Hg in the liver and kidney of these animals [mink and otter] suggests that a demethylation mechanism is present."
- "Demethylation of toxic organic Hg has been reported for some fish-eating birds, several species of marine mammals, raccoons, and mink (Freeman and Horne 1973; Jernelov et al. 1976; Norheim and Froslie 1978; Wren et al. 1980). The generally lower proportion of organic Hg in liver and kidneys of otter suggests that they possess a more efficient demethylating mechanism than do mink."
- "Mink are highly opportunistic predators, so their diet varies with location and time of year. Major food items of mink include fish, small animals, crayfish,

birds, and amphibians (Linscombe et al. 1982). The diet of otters is more monotonous and consists of at least 95% fish (Toweill and Tabor 1982)."

The literature indicates that, among duck species, the fraction of mercury in vegetarian mallards that is the more toxic form, methylmercury, is higher than in the piscivorous mergansers. This is actually the opposite of what might be expected when considering that nearly all of the mercury in fish is methylmercury while the fractions of methylmercury in plant and invertebrate mercury are much lower. Fimreite (1974) speculates that the observed difference may be attributable to methylating microflora in the guts of the vegetarians.

Another and probably more significant factor is that a demethylating mechanism is likely at work in piscivores. The ability to demethylate is how a piscivorous species may have evolved protection against toxic effects from the naturally high levels of mercury in fish. Non-piscivorous species, on the other hand, would have had no reason to evolve such a mechanism.

The above literature and some more recent literature provide evidence that demethylation occurs and that the demethylating mechanism tends to be more efficient as fish are more important in the species' diet and/or as the fish consumed by the species are higher in the food chain. Hence, cats are apparently more sensitive to mercury than mink, mink are apparently more sensitive to mercury than otters, and terrestrial mammals are apparently more sensitive to mercury than marine mammals. In each case, the sensitivity is reflected in the ratio of methylmercury to inorganic mercury in their tissues, which probably reflects their demethylation capability.

NJattach1

# Implementation of EPA's Methylmercury Criterion for Fish Tissue

# **FINAL REPORT**

Prepared by:

#### AMEC Earth & Environmental

and

#### ENVIRON

Prepared for

American Forest and Paper Association American Petroleum Institute Association of Metropolitan Sewerage Agencies U.S. Steel Utility Water Act Group

The Electric Power Research Institute (a research and development organization) also provided technical and financial support for this project

January 24, 2003

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#### **Executive Summary**

The Environmental Protection Agency's (EPA's) approach to managing exposures to methylmercury through consumption of self-caught fish in United States (U.S.) lakes and rivers has taken the form of a methylmercury criterion for fish tissue and pending guidance for implementation by states and tribes. The intent of this report is to provide EPA with recommendations on the development of its pending guidance. It is organized into four sections, as follows:

- Section 1 offers an introduction that, along with Appendix A, describes the basis for EPA's criterion for methylmercury exposure;
- Section 2 describes how states and tribes may make site-specific adjustments to EPA's criterion for fish tissue;
- Section 3 addresses how determinations might be made as to whether the methylmercury criterion has been exceeded; and
- Section 4 describes how the criterion might be implemented through the regulatory process.

In essence, sections 2 and 3 deal with criterion adjustment and Clean Water Act (CWA) § 303(d) listing issues. Section 4 deals with the implementation of the fish tissue criterion at the state level<sup>1</sup> and thus, involves issues such as translation of the tissue-based criterion into a water column-based criterion and the associated issues of total maximum daily loads (TMDLs), load allocations, and permit limits applicable to specific water bodies and dischargers.

Key findings and recommendations of this report are summarized below:

#### Site-Specific Criterion Adjustments

EPA recommends a fish tissue-based criterion to protect people from exposure to methylmercury. This approach is appropriate because there are no significant sources of exposure to methylmercury other than from fish consumption. A fish tissue criterion provides a more direct calculation of exposure than provided by use of a water column criterion, because the former reduces the need to deal with uncertainties in the relationship between water column concentrations and fish tissue concentrations.

EPA's criterion of 0.3 mg-methylmercury / kg of fish tissue is based on the average rate of consumption of freshwater and estuarine fish by recreational fishers, adjusted for methylmercury exposures due to consumption of marine fish. This criterion, based on national average consumption rates, can be adjusted based on consumption data specific to a water body of concern. EPA has defined a hierarchy of preferred fish consumption data sources based on specificity of the data to the water body of interest. The first preference is to use site-specific data. The second preference is to use data

<sup>&</sup>lt;sup>1</sup> For purpose of convenience, this report assumes that states will adopt EPA's 0.3 mg/kg recommendation and trophic level weighting procedure in their water quality standards regulations. States are authorized to adopt scientifically defensible alternatives (*see* 40 CFR §131.11(b)).

from similar populations or geographies. The third preference is to use data for similar populations based on national food intake surveys. The fourth preference is to rely on the default values used to derive the fish tissue criterion of 0.3 mg/kg.

The adjustment factor with the largest potential to affect the fish tissue criterion is the consumption "rate" of freshwater/estuarine fish from a specific water body. Other valuable consumption data include the consumption "distribution" by fish species or trophic level. The consumption distribution permits one to use site-specific weights for the types of fish consumed rather than default values based on U.S. averages. Finally, the consumption of marine fish by people who also consume fish from a specified fresh water body, if known, can be used to adjust the allowance for such consumption. This adjustment, referred to as the relative source contribution, affects the site-specific fish tissue criterion.

When using site-specific consumption data to make adjustments to the criterion, it is appropriate to use average values for consumption. The default criterion is based on EPA's best estimate of average consumption for sport fishers, so it is consistent to use average values for consumption at a specific site.

Determining Whether The Criterion Has Been Exceeded At A Site

To determine whether the fish tissue criterion has been exceeded in a lake, river, or estuary, the average fish tissue concentration, weighted by distribution of consumption by trophic level or species, should be compared to the criterion. This consumption distribution may be based on the default breakouts of consumption by trophic levels recommended by EPA, or distributions based on site-specific data of consumption by trophic level, species and/or fish size.

The use of average concentrations is appropriate because the methylmercury criterion is used by EPA as an acceptable level of exposure on a daily basis over a lifetime. Use of upper-end concentrations should be used only for acute health risks, which is not the case for methylmercury.

Where site-specific information is being collected, creel studies or fish sampling should reflect information about local variability of consumption. This includes temporal and spatial variability of consumption. Fish samples should be representative of times and locations where people catch fish from a given water body for consumption.

Water column or sediment concentrations should not be used to determine whether the fish tissue criterion has been exceeded for purposes of placing a water body on a state's § 303(d) list. This would require the translation of water column or sediment concentrations to fish tissue concentrations based upon bioaccumulation factors (BAFs) or other models of bioaccumulation. Bioaccumulation models are highly uncertain and EPA decided to set a fish tissue-based criterion to avoid their use.

Criterion Implementation through the Regulatory Process – Recommendations for Improvement

This section begins with a discussion of how the fish tissue criterion is being implemented in various stages of the regulatory process. It then highlights the technical challenges associated with those efforts, including dealing with the uncertainties in the mercury methylation process, sampling and analytical procedures, the bioaccumulation processes, the BAF in particular, and the watershed modeling process. This discussion of the state-of-the-science forms the basis for the recommendations detailed in the report and summarized below.

EPA and other organizations should conduct comprehensive studies to address the numerous gaps and other uncertainties regarding mercury fate and transport. Until such research is done, it is premature to attempt to translate a fish tissue-based criterion to a water column-based criterion. That research should combine laboratory, modeling, and field evaluation projects. For instance:

- If EPA wishes to establish water column-based criteria for total mercury based on methylmercury in fish, it needs to verify its assumptions regarding the constant proportionality between total and methyl mercury in the water column within a given water body. This is especially important in individual TMDLs;
- Laboratory mesocosm studies could be conducted to study food chain biomagnification of methylmercury in the presence of varying levels of dissolved organic carbon (DOC), pH, salinity or other environmental factors. Based upon the results, models could be constructed. Models should be tested by acquiring data and determining how well they are able to predict real-world results;
- An important element missing from EPA's TMDL sampling efforts to date is consideration of the food web structure that supports fish populations, and its vital role in determining mercury concentrations in fish. Because the feeding habits and food web structure vary considerably between different aquatic ecosystems, a careful evaluation of the food web is necessary to determine which sources (e.g., water, air, sediment) need to be managed in order to reduce mercury levels in fish in specific water bodies.

Considerable time and effort will be necessary to complete the research described in this report. In the interim, EPA and the states can move forward with various activities that will lead to effective mercury reduction strategies. Following are some observations and recommendations in that regard.

- It will take many years (>10 years) before scientifically-defensible TMDLs can be developed;
- Where TMDLs must be initiated before adequate research or site-specific data collection can be completed (*e.g.*, due to a court-ordered schedule), a phased TMDL should be performed;
- Phased TMDLs should not attempt to translate fish tissue criteria (or reference doses (RfDs)) into water column-based water quality standards;

- Load reductions should not be imposed on point sources until such time as a linkage can be established between a discharge and a water quality impairment; discharge of inorganic mercury into a water body in trace quantities does not establish such a linkage;
- EPA should perform additional studies to investigate specific and demonstrable linkages between current atmospheric deposition and mercury in ambient water and fish tissue;
- Monitoring plans should be established in an attempt to determine the linkage between loads and water quality impairments;
- Monitoring plans should be developed and implemented to establish water quality trends, including fish tissue trends, which will serve as a basis for measuring the success of mercury load reduction efforts;
- Monitoring plans should be developed and implemented in order to identify the relationship between load reduction and ecosystem (especially fish) response; and
- In systems where fluvial processes (i.e. runoff and erosion) dominate loadings to the water body, TMDLs initially should focus on the collection of data to identify the amount of mercury contributed by atmospheric, terrestrial (anthropogenic or natural background) and point sources. Without such information for a given watershed, it is impossible to realistically establish required load reductions, allocate load reductions, or estimate time frames required to attain the standard.

If EPA or states decide to derive a water column-based criterion from a fish tissue criterion or RfD, it is recommended that a model with some degree of scientific sophistication, such as the Electric Power Research Institute's (EPRI's) Mercury Cycling Model, be used to model aquatic fate and biological uptake. It is not recommended at this time that simple models utilizing BAF or sediment BAF (SBAF) concepts be used to derive water column-based criteria from fish tissue-based criteria. However, if EPA or states decide to rely on BAFs, we recommend the following:

- Site-specific studies of 3-5 years' duration should be conducted to establish BAFs;
- A sampling plan along the lines presented in this document should be developed and implemented;
- Research should confirm that none of the assumptions underlying the use of the BAF concept have been violated;
- Accurate creel surveys of the water body should be conducted to support an assessment of fish caught and consumed (quantity and species) from the water body;
- Resulting BAFs gathered from such studies should be weighted by trophic level or by species caught and consumed in order to set water quality targets. While weighting by trophic level as was done in establishing the methylmercury criterion is a step in the right direction, weighting by specific species caught and consumed is preferable due to the variability of mercury tissue burdens among species in the same trophic level, even within a similar age class; and
- Data should be analyzed so that error and bias are minimized in resulting calculations. This includes validating appropriate test methods so that users can know the interlaboratory performance characteristics that those methods are expected to exhibit.

#### 1.0 Introduction and Overview

Environmental exposures to mercury, especially in the form of methylmercury, have been receiving increasing attention over the past decade. In response to requirements in the 1990 Clean Air Act (CAA) Amendments, the U.S. Environmental Protection Agency (EPA) prepared the November 1997 Mercury Study Report to Congress (US EPA 1997a), which reported that approximately 7 percent of United States' women of childbearing age were exposed to methylmercury at levels in excess of the reference dose (RfD). The Utility Air Toxics Report to Congress, published in February 1998, identified mercury as the utility air toxic of greatest concern. Throughout the 1990's, large epidemiological studies of populations exposed to levels of methylmercury higher than those of the U.S. population were conducted. These studies were reviewed in a report from the National Research Council published in 2000 (see Appendix A). Based on these studies and the recommendations of the National Research Council committee, the EPA published a new RfD for methylmercury in July 2001 (US EPA 2001a). While the RfD was unchanged from the previous value of 0.1 µg/kg-day, its publication focused attention on mercury and methylmercury.

Throughout the period of these studies, the number of fish advisories based on measured methylmercury levels was increasing. These advisories, issued by states, took various forms, but most were designed to protect women of childbearing age from consuming too frequently fish likely to have methylmercury concentrations above certain levels.

All of these factors have led to efforts to further control mercury releases; thus, decreasing exposures to methylmercury. While the majority of exposures of the U.S. population to methylmercury are due to the consumption of commercially purchased marine fish, U.S. regulatory agencies have little control over the sources that contribute to concentrations in marine fish. The U.S. Food and Drug Administration limits the concentration of methylmercury in marine fish available for sale to 1 mg/kg, and also has issued an advisory to pregnant women (US FDA 2001). This advisory recommends that pregnant women do not consume shark, swordfish, king mackerel, and tilefish, and that consumption of other fish by pregnant women be limited to an average of 12 ounces, cooked weight, per week.

EPA's approach to managing exposures to methylmercury through consumption of selfcaught fish in U.S. lakes and rivers has taken the form of a Clean Water Act (CWA) § 304(a) methylmercury water quality criterion based on fish tissue concentrations and pending guidance for implementation by the states and tribes.<sup>2</sup> The intent of this report is to provide EPA with recommendations on the development of its pending guidance. This report is organized into four sections, as follows:

 Section 1 is an introductory section that, along with Appendix A, describes the health basis for EPA's evolving regulatory program to limit methylmercury exposures;

<sup>&</sup>lt;sup>2</sup> For purpose of convenience, this report assumes that states will adopt EPA's 0.3 mg/kg recommendation and trophic level weighting procedure in their water quality standards regulations. States are authorized to adopt scientifically defensible alternatives.

- Section 2 describes how to make site-specific adjustments to EPA's criterion for fish tissue, based on site-specific data. The primary types of site-specific data that are used to make these adjustments concern the types and amounts of fish consumed, both from local lakes and rivers and also from marine sources. Where the site-specific information indicates that the default values relied on by EPA are not representative of a local situation, examples are provided indicating how such information can be used to establish a site-specific value;
- Section 3 identifies several approaches for determining whether the methylmercury concentrations in fish tissue from a specific water body are above or below the criterion; and
- Section 4 discusses the regulatory implications associated with a determination that the applicable fish tissue level has been exceeded.

#### 1.1 Basis for the Updated RfD

For health risks other than cancer, EPA limits exposures to hazardous substances through the use of a reference dose (RfD), which it defines as a level of oral intake that "is likely to be without an appreciable risk of deleterious effects during a lifetime." (US EPA 2001a). The RfD for methylmercury is 0.1 µg/kg-day, and has been this value for several years. However, EPA recently has revised the basis for this RfD. The change in the basis for the RfD is due to the publication of several epidemiological studies of the performance of children exposed *in utero* to levels of methylmercury that are high in comparison to typical U.S. exposures.<sup>3</sup> The EPA revisions to the RfD were made in response to recommendations from a committee of the National Academy of Sciences that the RfD be updated based on a study of children in the Faroe Islands (Committee on the Toxicological Effects of Methylmercury 2000). Details and discussion of how the RfD was derived are provided in Appendix A.

#### 1.2 Derivation of the 0.3 mg/kg Fish Tissue Criterion

The basic health protection criterion is provided by the methylmercury RfD, which is 0.1  $\mu$ g/kg-day. For a 70 kg person, this is equivalent to 7  $\mu$ g/day intake, or 50  $\mu$ g/week, or 210  $\mu$ g/month. To make this exposure level more easily implemented for specific water bodies, EPA developed a derivative water quality criterion based on non-exceedance of the RfD. EPA's *Water Quality Criterion for the Protection of Human Health: Methylmercury* derives a fish tissue concentration of 0.3 mg/kg (equivalent to 0.3  $\mu$ g/g or 0.3 ppm (US EPA 2001b) as the concentration that should not be exceeded in ingested fish on average. Section 2 of this report provides details and examples of how the fish tissue criterion can be adjusted when site-specific information on consumption is available or can be obtained.

The full details of this derivation are provided below in Section 2.1. In brief, the fish tissue concentration value is based on consumption of 17.5 g/day of freshwater fish.

<sup>&</sup>lt;sup>3</sup> To illustrate the differences, the methylmercury concentrations measured in maternal hair in the Faroe Islands study ranged from 2.5 to 7.4 ppm, with a geometric mean concentration of 4.1 ppm (Committee on the Toxicological Effects of Methylmercury, 2000). In contrast, the median concentration in U.S. women in a recent study (CDC, 2001) was 0.2 ppm.

Consumption of 17.5 g/day of fish with 0.3 mg/kg methylmercury would produce an exposure rate of 5.25  $\mu$ g/day. In the derivation of the 0.3 mg/kg value for fish tissue concentration, EPA recognized that people consume both freshwater and marine fish, and that methylmercury exposures occur for both sources. To account for exposures from marine fish, EPA assumed a methylmercury intake of 1.89  $\mu$ g/day from marine fish. EPA's basis for this estimate is described in Section 2.1.2.

The 0.3 mg/kg fish tissue criterion is derived based on the total estimated consumption of freshwater fish, adjusted upward to account for methylmercury exposures from marine fish consumption. However, it is known that methylmercury concentrations are not uniform across different fish species, but tend to increase with trophic level, (i.e., different levels of the aquatic food chain), with the highest methylmercury levels typically found in top predator fish. To allow for creation of a weighted average for fish at different levels of the aquatic food chain, EPA provided an estimate of the trophic levels of fish consumed that make up the estimated total consumption rate of 17.5 grams per day. The breakdown of the 17.5 g/day consumption by trophic level is 3.8 g/day of trophic level 2 fish, 8 g/day of trophic level 3 fish, and 5.7 g/day of trophic level 4 fish. EPA indicates that these estimates are derived from the Agriculture Department's 1994-96 Continuing Survey of Food Intake by Individuals (CSFII) survey (US EPA 2000b).

#### 1.3 EPA's Approach vs. Current State Approaches

Until states adopt a fish tissue criterion into their water quality standards regulations, either EPA's value or a scientifically-defensible alternative, many will rely on fish consumption advisories to address excessive methylmercury exposure. Once states adopt a fish tissue criterion, some may continue to use fish advisories as a public information tool, especially for sensitive sub-populations that their fish tissue criterion may not be suited to protect. Limiting exposures through the use of fish advisories is not specifically addressed in this report.

#### 2.0 Site-Specific Criterion Adjustments

This section explains EPA's basis for deriving its methylmercury criterion in fish tissue (2.1), describes options for seeking site-specific adjustments of that criterion (2.2), and explores options for collecting the information necessary to support a site-specific criterion (2.3).

#### 2.1 Introduction on the Basis for EPA's Methylmercury Criterion

EPA relies on the RfD as its basis for protection of human health. If exposures do not exceed the RfD of 0.1 µg/day-kg body weight or 7 µg/d for a 70 kg person, EPA states that human health is protected (US EPA 2001a). In order to ensure that the population is not exposed to methylmercury in amounts exceeding the RfD, guidance for determining exposure is required. Exposure calculations for developing a fish tissue criterion are included in EPA's *Water Quality Criterion for the Protection of Human Health: Methylmercury* (US EPA 2001b). The calculations are based on guidance provided in EPA's *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (US EPA 2000a). The final report of the Exposure Assessment Technical Support Document for the Methodology will not be published until 2003. Therefore, references to exposure assessment issues covered by the Technical Support Document refer to the final draft published in July 1998 (US EPA 1998a).

Because the methylmercury criterion is pursuant to § 304(a) of the Clean Water Act, exposure guidance focuses on the pathways of ambient and drinking water intake and freshwater and estuarine fish consumption. This guidance is discussed in Section 2.1.1; but briefly, § 304(a) requires the EPA Administrator to establish "criteria for water quality accurately reflecting the latest scientific knowledge ... on the kind and extent of all identifiable effects on health and welfare ... which may be expected from the presence of pollutants in any body of water." In the case of methylmercury, EPA has based its water guality criterion on the methylmercury RfD, taking into account all exposure pathways. To determine total exposure for comparison to the RfD, calculation of exposure from intake pathways in addition to exposure from fish consumption is necessary. This calculation is referred to as the relative source contribution (RSC) and is discussed in Section 2.1.2. In addition, the population that the criterion is meant to protect can be defined in various ways resulting in widely different estimates of exposure to methylmercury. The choice of the population of concern is addressed in Section 2.1.3. The results of combining exposure guidance and the relative source contribution for the population of concern are summarized in Section 2.1.4. This section shows how EPA calculates a water quality criterion of 0.3 mg/kg in fish tissue.

#### 2.1.1 Exposure Guidance

The ambient water quality criterion (AWQC) for methylmercury is derived to limit methylmercury exposure from all pathways to rates consistent with the RfD. Based on many years of study, EPA has determined that fish consumption is the primary pathway for methylmercury exposure. As a result, EPA developed a fish tissue criterion to protect people from excessive exposure to methylmercury in fish caught from freshwater or

estuarine water bodies (US EPA 2001b). EPA issued guidance explaining its rationale for calculating this exposure (US EPA 2000a).

EPA determined that contact with water and ingestion of drinking water make negligible contributions to methylmercury exposure relative to exposure from consumption of fish. Using available data, EPA estimated that exposures from water contact and drinking water are orders of magnitude below exposures from freshwater and estuarine fish (US EPA 2001b, Section 5.7.4). Therefore, the water quality criterion for methylmercury is based on exposures from freshwater and estuarine fish, as discussed below in Section 2.1.2.

Unlike the water quality criteria guidance for many other substances, EPA has chosen to use a fish tissue criterion, instead of a water concentration criterion for methylmercury. The fact that exposure from drinking water is negligible permits this approach and, by using a fish tissue criterion, EPA can avoid, to a degree, dealing with the uncertainties in the relation between water column concentrations and fish concentrations. The use of a fish tissue criterion provides for a more direct linkage between fish concentrations and the receptor being protected, allows better resolution in calculations of exposure, and allows adjustments for site-specific variability that would be difficult to accommodate with a water column-based approach. This approach also allows exposure guidance to be based solely on calculations of exposure from eating fish. However, it places a burden on the states and tribes who must deal with the uncertainties in the relation between water column concentrations and fish concentrations when they implement the criterion for various regulatory applications.

The factors that are considered in determining exposures to methylmercury from consumption of freshwater/estuarine fish are the consumption rate and the methylmercury concentration of the fish consumed. Calculation of methylmercury exposure is simply the product of the two factors.

The consumption rate may include consideration of consumption frequency and portion size. The default consumption rate of freshwater/estuarine fish recommended by EPA is 17.5 grams/day for the general population of fish consumers (US EPA 2000a, Section 4.3.3.1). Calculation of an alternative to this default value requires information on consumption frequency and portion size. For a portion size of 8 ounces (227 grams), the default consumption rate translates to a consumption frequency of 0.08 portions per day or about one portion every 13 days.

The value used for the concentration of methylmercury in fish needs to be representative of the variety of fish consumed. Methylmercury concentrations in fish vary widely by species, size, and trophic level. This means that the concentration should be based on the proportion of each type or trophic level of fish consumed. The generalized equation for average concentration, weighted for trophic level, is as follows:

$$C_{avg} = \frac{\sum_{i=2}^{4} FI_{i}C_{i}}{\sum_{i=2}^{4} FI_{i}}$$
(2-1)

where

- i = Trophic level number for fish (i=2,3,4)
- Fl<sub>i</sub> = Fish consumption at different fish trophic levels (g/day)
- C<sub>i</sub> = Concentrations at different fish trophic levels (mg/kg)

The default trophic level breakouts recommended by EPA are 3.8 grams per day for trophic level 2 fish, 8.0 grams per day for trophic level 3 fish, and 5.7 grams per day for trophic level 4 fish. The default equation for calculation of the average tissue concentration is as follows:

$$C_{avg} = \frac{3.8 \times C_2 + 8.0 \times C_3 + 5.7 \times C_4}{17.5}$$
(2-2)

Consumption data, when available, may be used instead of these default breakouts. Site-specific data can be used in place of the default values for the mix of trophic level fish or for a specific mix of fish on a species-by-species basis. In addition, the default consumption rate could be replaced with site-specific or regional data. In general, the objective should be to ensure that exposures in excess of the methylmercury RfD do not occur, considering an appropriate database in terms of quality and quantity.

#### 2.1.2 Relative Source Contribution

The exposure EPA considered in deriving its fish tissue criterion was adjusted for sources other than the consumption of freshwater/estuarine fish. In general, these other sources include air inhalation, soil ingestion, ingestion of food other than seafood, and consumption of marine fish. The accounting for other sources is based on a calculated ratio, the relative source contribution (RSC). The RSC is the quantity of methylmercury exposure due to consumption of marine fish, relative to all sources combined. As noted above, EPA determined that exposures to methylmercury from sources such as the air, soil, and non-seafood diet are negligible relative to the RfD, and relative to exposure from fish. Therefore, the RSC for methylmercury is based on exposure from consumption of marine fish.

Like exposure from freshwater/estuarine fish consumption, exposure from consumption of marine fish is based on the product of the consumption rate of marine fish and an average methylmercury concentration in marine fish. The default consumption rate for consumption of marine fish recommended by EPA is 12.46 grams per day. The recommended weighted-average concentration of methylmercury in marine fish is 0.157 mg/kg, which is based on a species-weighted average methylmercury concentration in marine fish, derived from data from the National Marine Fisheries Service (US EPA 2001b, Table 5-16). This results in an estimated default intake of 1.89 µg/day from consumption of marine fish.<sup>4</sup> Different consumption rates of marine fish may be appropriately derived using data from local surveys, from surveys of similar populations,

<sup>&</sup>lt;sup>4</sup> Actually, 12.46 x 0.157 = 1.96, not 1.89. Apparently EPA divided by a body weight slightly above 70 kg (the Exposure Factors Handbook value for adults is 71.8 kg) and rounded the result to 0.027  $\mu$ g/kg-d. When 0.027  $\mu$ g/kg-d is converted back into units of daily intake based on a 70 kg body weight, the result is 1.89  $\mu$ g/d. For the single-digit precision of the tissue criterion, the small differences in body weight and rounding do not affect the result; the RSC comes out at 0.3 mg/kg if 0.196  $\mu$ g/d is used.

or from regional differences in national surveys. For example, the Agriculture Department's Continuing Survey of Food Intake by Individuals (CSFII) data indicate that, on average, residents near the East or West coasts consume more fish on a per capita basis than residents in the Midwest. It is possible, in theory, to adjust the RSC to account for concentrations of methylmercury in marine fish consumed by a local population that differs from that of EPA's default value. This adjustment may prove difficult to make in practice, absent additional data.

An additional adjustment factor that may prove to be of increasing importance is the consumption of farm-raised fish. The literature indicates that farm-raised fish usually have low concentrations of methylmercury. However, the consumer may not know whether the salmon consumed at a restaurant or purchased at a grocery store is wild or farm-raised, and this may be accounted for inappropriately by the RSC for marine fish consumption. If the consumption rate and/or the weighted-average concentration are different from those assumed in the default RSC value, an alternative value for exposure resulting from marine fish can be calculated and the RSC revised.

The sum of exposures to methylmercury from consumption of freshwater/estuarine fish and exposures from marine fish is compared with the RfD. To calculate the water quality criterion applicable to freshwater fish, the marine fish exposure (RSC) is subtracted from the RfD. The remaining portion of the RfD is the allowable exposure from freshwater/estuarine fish. EPA concludes that the water quality criterion is the maximum concentration that results in an exposure less than or equal to the RfD.

The decision to use the subtraction method for the RSC follows the Exposure Decision Tree for Defining Proposed RfD Apportionment given in the Methodology, (US EPA 2000a, Fig 4.1) Using the subtraction method, non-site-specific intakes are subtracted from the total exposure that can occur consistent with the RfD. The exposure decision tree is reproduced on the following page.

EPA used the exposure decision tree for methylmercury, as follows:

- Box 1: EPA identified the population of concern as described in Section 2.1.3;
- Box 2: EPA identified the exposure pathway as primarily fish consumption as described above in Section 2.1.1;
- Box 3: EPA determined that adequate data are available to describe relevant exposure intakes. This determination sends the decision to Box 9;
- Box 9: EPA estimated that the total exposure to methylmercury for the average recreational fisher is 0.092 µg/kg-day, which is 92% of the RfD of 0.1 µg/kg-day. This total exposure is close enough to the RfD that the answer is Yes, which sends the decision to Box 10;
- Box 10: The Box 9 result means that a final decision on apportionment by risk managers should consider other issues such as cost and feasibility concerns in addition to apportionment estimates by the method determined by Box 11. In the case of methylmercury, EPA decided on apportionment that does not deviate from the apportionment method determined by Box 11;
- Box 11: EPA determined that there is only one health-based criterion to apportion, the answer is No and the subtraction method described in Box 12 is used; and

Box 12: If the intake from sources other than the source of concern is between 20% and 80% of the RfD, then the intake from the other sources is the relative source contribution (RSC). Since methylmercury intake from marine fish consumption is about 27% of the RfD, this amount is subtracted from the RfD to determine the allowable exposure from freshwater/estuarine fish, which is 73% of the RfD or 0.073 µg/kg-day. Subtracting the RSC of 1.89 µg/day from the RfD for a 70 kg adult of 7 µg/day results in 5.11 µg/day as the default allowable methylmercury intake from the source of concern, freshwater/estuarine fish.



Exposure Decision Tree for Defining Proposed RfD (or POD/UF) Apportionment

As detailed above, the RSC is based on consumption of marine fish and the average concentration of methylmercury in these fish. Any change to the RSC based on different consumption rates or concentrations in marine fish will affect the maximum exposure allowed from freshwater/estuarine fish and, therefore, the water quality criterion. For example, if different values for marine fish intake produce a RSC that is less than 1.89  $\mu$ g/d, subtracting the new value from the RfD of 7  $\mu$ g/d will result in allowable intake from freshwater/estuarine fish higher than 5.11  $\mu$ g/d. Exposure equaling the RfD would then occur at freshwater/estuarine fish concentrations higher than the 0.3 mg/kg criterion. The reverse case, where a higher RSC would require a lower criterion, also is true.

#### 2.1.3 Population to be Protected

In order to calculate exposure, the population of concern needs to be defined. The water quality criterion is meant to protect this population from adverse health effects resulting from intake of methylmercury. There are two steps in defining the population for which exposure is calculated. First, the population subgroup to be protected is chosen. Second, representative exposure values and other factors such as body weight are determined for the population subgroup.

#### 2.1.3.1 Choosing the Population to be Protected

Quantifying exposure depends on the population to which the exposure calculations apply. Therefore, the determination of an AWQC depends on the choice of the particular population to protect. As a starting point, the AWQC is evaluated based on default intake values for the chosen population subgroup. EPA provides recommendations for default values for the following five populations: adults in the general population, sport fishers, subsistence fishers, women of childbearing ages, and children (US EPA 2000a, Section 2.1). As discussed in Appendix A, Chapter 5 of EPA's Water Quality Criterion for the Protection of Human Health directs that the methylmercury RfD applies to children and adults of both genders, even though the RfD is based on effects of children exposed in utero (US EPA 2001b). EPA determined that there are inadequate data supporting the derivation of a child RfD; therefore, the criterion is developed for the general adult population. Regarding exposures to children, the EPA *Exposure Factors* Handbook. Table 10-17, indicates that the mean intake rate of freshwater and estuarine fish by children under 14 years of age, in units of mg/kg-day, is not higher that that of adults (US EPA 1997b). In contrast, preliminary results from the Center for Disease Control's (CDC's) 1999 National Health and Nutrition Examination Survey (NHANES) study indicate that methylmercury concentrations in blood and hair are significantly lower in children than in women (CDC 2001). EPA used the relevant default values for adults in the general population to calculate the criterion.

Exposure data, such as fish consumption and fish concentrations, should be representative for the population to be protected. EPA applies the methylmercury RfD to the general population; but, the only exposure pathway for users of a water body is from fish consumption. Therefore, the consumers of fish caught in a water body make up the population of concern for that water body. This is consistent with the CWA, which aims to protect the beneficial uses of a water body. In this case, the beneficial use is fishing. When using alternatives to the default values recommended by EPA, one may work

directly with the data on consumption and on the methylmercury concentration of fish in a particular water body without categorizing the population group as sport fishers or subsistence fishers. However, if the data are not sufficient to provide consumption and concentration values for users of the water body, the data may be able to differentiate the users of a water body as representing the general population, sport fishers, or subsistence fishers. In this case, default values for the appropriate categories may be an improvement from the default value used by EPA in setting the criterion.

#### 2.1.3.2 Mean Consumption vs. Upper End of Consumption Distribution

In choosing exposure values representative of the population of concern, EPA's guidance is flexible. In Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health (US EPA 2000a), EPA says, "State and authorized Tribes may use either high-end values (such as 90th or 95th percentile values) or average values for an identified population that they plan to protect (e.g., subsistence fishers. sport fishers, or the general population)." In recommending a default fish consumption rate of 17.5 grams/day for protecting the general population, EPA uses a value representing the 90<sup>th</sup> percentile of the value for freshwater and estuarine fish from the 1994-1996 CSFII conducted by the Agriculture Department (US EPA 2000b). When recommending default fish intake rates for recreational and subsistence fishers of 17.5 grams/day and 142.4 grams/day respectively, EPA uses values representative of 90<sup>th</sup> and 99<sup>th</sup> percentiles of the general population. This reflects an informed judgment by EPA, as solid data on fish consumption by recreational and subsistence fishers are generally lacking. Based on this judgment, EPA considers those upper end values for the general population to be "indicative of the average consumption among sport fishers and subsistence fishers, respectively" (US EPA 1998a). The populations of concern for a water body are likely to be recreational and subsistence fishers.

#### 2.1.4 Calculation of Methylmercury Criterion

EPA states that its water quality criterion is set to ensure that exposure to methylmercury does not exceed the RfD. The criterion is intended to be calculated as the maximum concentration of methylmercury in freshwater/estuarine fish that results in exposure not exceeding the RfD. This calculation consists of default values for consumption of freshwater/estuarine fish (exposure guidance) and exposure to methylmercury from marine fish (RSC calculation) for the population of concern.

As presented in Section 7.0 of the Methylmercury Water Quality Criterion document (US EPA 2001b), the equation for calculating the methylmercury fish tissue residue criterion is:

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI_i}$$

(2-3)

where

TRC = Fish tissue residue criterion (mg-methylmercury / kg-fish) for freshwater and estuarine fish,

RfD = Reference dose (based on non-cancer human health effects) of 0.0001 mgmethylmercury / kg-body weight-day,

RSC = Relative source contribution (subtracted from the RfD to account for marine fish consumption) estimated to be 2.7 x 10<sup>-5</sup> mg-methylmercury / kg-body weight-day,

BW = Human body weight default value of 70 kg (for adults), and

FI = Fish intake at trophic level (TL)<sub>i</sub> (i = 2, 3, 4); total default intake is 0.0175 kg fish/day for the general adult population.

Using default values, the criterion for the general population and sport fishers is calculated as follows.

$$TRC = \frac{70 \, kg \times (0.0001 \, \frac{mg}{kg \cdot d} - 0.000027 \, \frac{mg}{kg \cdot d})}{0.0175 \, \frac{kg}{d}} = \frac{5.11 \, \frac{mg}{d}}{0.0175 \, \frac{kg}{d}} = 0.292 \, \frac{mg}{kg}$$
(2-4)

The recommended criterion of 0.3 mg/kg is rounded from this result.

In evaluating whether exposures exceed the fish tissue criterion in specific water bodies, fish tissue concentrations need to be weighted by the appropriate trophic level breakouts. In making adjustments to the fish tissue criterion, the fish intake values and relative source contribution calculation are the most likely to be updated based on site-specific data.

#### 2.2 Technical Bases for Regional or Site-Specific Adjustments

Estimates of a population's exposure to methylmercury may be more applicable to a specific population than are the default values. If such estimates are available or are developed, regional or site-specific adjustments can be made. The default values for parameters such as consumption rate and the RSC estimate may not represent accurately regional or local conditions or the specific population of concern. If so, the criterion will not equal the maximum concentration in fish resulting in exposures equaling the RfD as intended. As a result, EPA "strongly encourages States and authorized Tribes to consider developing a criterion using local or regional data over the default values if they believe that they would be more appropriate for their target population" (US EPA 2001b).

In the 2000 human health methodology (US EPA 2000a), EPA established a hierarchy of data sources that can be used to make adjustments to fish intake assumptions used in the derivation of the criterion. The first preference is to use data applicable to the specific water body of concern. The second preference is the use of data reflective of similar geography and population groups. The third preference is to use data for different population groups based on national food intake surveys. The fourth preference is to use the default values that support the 0.3 mg/kg fish tissue criterion.

This hierarchy can be used for any of the exposure parameters used to calculate the fish tissue criterion. If the data are adequate, using data in the higher preferred categories (e.g., intake data from the water body of concern) for any exposure parameter results in an estimate of exposure more representative of the population of concern. Adjustments using this hierarchy can relate to more accurate information on consumption of fish from the water body of concern, including information on size, type, and trophic level of fish consumed, and consumption of marine fish.

In theory, one also could consider information about BAFs and toxicology; in practice this is not likely to prove helpful. BAFs, discussed in Section 4, are used to estimate the relationship between mercury entering a lake or river and the concentration of methylmercury in fish. BAFs come into consideration when remedies are sought to lower the mercury concentration in fish and in water bodies (i.e., through regulatory implementation). But, because EPA has based its process for protecting the public on more direct measures of exposure such as the 0.3 mg/kg fish tissue criterion, BAFs are not a consideration in making site-specific adjustments to the criterion.

Similarly, in principle the EPA Regional Offices will consider information suggesting that the toxicological information in the Integrated Risk Information System (IRIS) is incorrect or inappropriate in a particular circumstance. In this case, states can present alternative values of a scientifically defensible RfD for review by the EPA. However, EPA has not endorsed this type of adjustment to the same degree as adjustments based on site-specific exposure due to the level of effort that has been expended on methylmercury toxicity over the past several years and the degree of peer review and participation by external groups, such as the National Research Council committee.

#### 2.2.1 Adjustments Based on Site-Specific Consumption Information

States and tribes can use site-specific consumption data to develop a site-specific fish tissue criterion. This criterion will represent the highest average fish concentration that will protect the health of users of a particular water body, given their consumption of fish caught in the water body. Consumption studies, such as those performed at San Francisco Bay (SFEI 2000) or Lake Ontario (Connelly et al 1996), can provide the necessary site-specific data to use in place of the 17.5 g/day generic freshwater/estuarine fish consumption used in the fish criterion calculation. Use of a site-specific consumption value results in a fish tissue concentration criterion more appropriate for the specific site than the default value of 0.3 mg/kg.

For example, mean consumption of San Francisco Bay fish was found to be 23 g/day, while mean consumption by Lake Ontario fisherman was found to be 4.9 g/day. If these are the only values in the criterion calculation that could be changed, the San Francisco Bay criterion would be lower and the Lake Ontario criterion would be greater than 0.3 mg/kg. The calculations for an adjusted criterion would be as follows for San Francisco Bay and Lake Ontario, respectively:

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI_{i}} = \frac{\frac{70 kg \times (10^{-4} \frac{mg}{kg \cdot d} - 2.7 \times 10^{-5} \frac{mg}{kg \cdot d})}{23 \frac{g}{d}} = 0.2 \frac{mg}{kg}$$
(2-5)

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI_{i}} = \frac{70 kg \times (10^{-4} \frac{mg}{kg \cdot d} - 2.7 \times 10^{-5} \frac{mg}{kg \cdot d})}{4.9 \frac{g}{d}} = 1 \frac{mg}{kg}$$
(2-6)

If the most preferred site-specific data (i.e., site-specific consumption data by fish type or trophic level) are not available and cannot reasonably be developed, the second preference is to use representative data based on similar geographies or populations. Often, statewide fish consumption surveys provide information that can be used to revise the freshwater/estuarine fish consumption value. This value then can be used to calculate an adjusted water quality criterion for a water body in the same state or region. Although not as preferable as a value based on site-specific data, using this value is more appropriate for the water body than using the default values, which are based on national consumption data.

A fish consumption study for Indiana sport fishers (Williams et al 2000) included samples at various fishing locations in Indiana. In addition, data were collected that indicated regional consumption differences in Indiana. In this study, mean consumption in the north region of Indiana was found to be 14.0 g/d, while mean consumption in the central region was found to be 28.6 g/d. If the freshwater/estuarine fish consumption is the only value that can be changed in the criterion calculation, criteria for water bodies in the north region would be greater than the default criterion and criteria for water bodies in the central region would be less than the default criterion. The calculations for an adjusted criterion would be as follows for the north region and the central region, respectively.

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI_{i}} = \frac{70kg \times (10^{-4} \frac{mg}{kg \cdot d} - 2.7 \times 10^{-5} \frac{mg}{kg \cdot d})}{14.0\frac{g}{d}} = 0.4 \frac{mg}{kg}$$

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI_{i}} = \frac{70kg \times (10^{-4} \frac{mg}{kg \cdot d} - 2.7 \times 10^{-5} \frac{mg}{kg \cdot d})}{28.6\frac{g}{d}} = 0.2 \frac{mg}{kg}$$
(2-7)
(2-8)

The third preference is to use distributional data from national food surveys. In setting the default values, EPA uses the CSFII. The CSFII has regional breakouts of fish consumption data, but EPA does not recommend use of those breakouts to represent regional consumption (US EPA 1998a). EPA's basis for this recommendation is that, for some regions, the data are insufficient to provide a solid basis for a regional adjustment In addition, EPA noted that some regions involve combinations of states in which the differences in consumption in the states in the region could be large. The breakout information specific to the region at issue would need to be assessed to determine whether the above concerns are valid.

The fish tissue criterion of 0.3 mg/kg is based on default values of freshwater/estuarine fish consumption. If adequate consumption data in the form of creel surveys or similar information are available or can be developed, use of the site specific consumption data more accurately quantifies the exposures resulting from the use of the water body. This is the top tier of data to be used, based on the EPA hierarchy described in Section 2.2. This more accurate quantification allows calculation of a fish tissue criterion that better allows use of the water resource while protecting the health of those who use a water body.

#### 2.2.2 Adjustments Based on Consumption Rates of Fish of Each Trophic Level

The default criterion of 0.3 mg/kg represents a fish tissue concentration that is averaged across all trophic levels; that is, it is a single concentration representing the average concentration of all fish consumed. However, methylmercury levels generally are higher in higher trophic level fish. As a result, exposure to methylmercury depends on the trophic levels of fish consumed in addition to the total quantity consumed. Therefore, it is possible to refine the fish tissue criterion to include information about consumption and concentration of methylmercury that is specific to each trophic level or to individual fish species or fish sizes. A site-specific adjustment to a fish tissue criterion can include an adjustment based on the available information, including details based on trophic level or species.

Consumption studies may detail consumption by species, and trophic level breakouts can be derived from the data. In some cases, (e.g. San Francisco Bay) consumption data may include species-specific information, but only with respect to how many anglers sampled consume different species. The data may not quantify the amount consumed of each species, so adjustments to the trophic level breakouts cannot be made. However, the information provided may justify a decision to collect data of species-specific consumption quantities.

For consumption studies such as the Lake Ontario or Indiana rivers studies that do not include information on the distribution of fish type consumed, the default assumptions regarding trophic level consumption still can be applied, normalized to the adjusted total consumption rate. This would be useful for the situation where tissue concentration data were available for each trophic level. For example, for sport fish consumption of Lake Ontario fishers of 4.9 g/d, the trophic level breakouts would be calculated as follows.

$$TL2 = 4.9 \frac{g}{d} \times \frac{3.8 \frac{g}{d}}{17.5 \frac{g}{d}} = 1.1 \frac{g}{d}$$

$$TL3 = 4.9 \frac{g}{d} \times \frac{8.0 \frac{g}{d}}{17.5 \frac{g}{d}} = 2.2 \frac{g}{d}$$
(2-9)
(2-10)

$$TL4 = 4.9 \frac{g}{d} \times \frac{5.7 \frac{g}{d}}{17.5 \frac{g}{d}} = 1.6 \frac{g}{d}$$
(2-11)

Trophic level breakouts can be derived from creel surveys. Creel surveys may not give information about per capita consumption of fish, but will show the amount of each fish species caught from a water body. Use of this information in developing site-specific trophic level breakouts assumes that the average distribution of fish consumed from a water body is similar to the distribution of fish harvested from the water body. This type of information was gathered in a creel survey done for southeastern Georgia rivers by the Georgia Wildlife Resources Division. An 8-month creel survey for the Atamaha River conducted in 2000 demonstrates how adjustments to the trophic level distribution portion of the criterion could be performed (Georgia Fisheries Management Section 2001). That survey found the following distribution:

Species	Trophic Level	Harvest Mass (kg)	Percentage by Mass
Largemouth Bass	4	639.11	2.3%
Redear Sunfish	3	1129.64	4.0%
Channel Catfish	3	5960.51	21.3%
Redbreast Sunfish	3	1190.88	4.3%
Bluegill	3	1801.63	6.4%
Black Crappie	3	415.43	1.5%
Flathead Catfish	4	8906.67	31.8%
Mullet	2	7423.71	26.5%
Warmouth	3	110.21	0.4%
Spotted Sunfish	3	72.53	0.3%
Other	3/4	319.87	1.1%
American Eel	3	15.92	0.1%

The trophic level breakout is 26% trophic level 2, 39% trophic level 3, and 35% trophic level 4 by weight. It is important to calculate the distribution based on mass because methylmercury intake is dependant on mass of fish consumed. As a result, the default breakouts are mass values and any adjustments should be treated similarly. The revised distribution based on the creel survey would be 26%, 39% and 35% of 17.5 g/day, equivalent to 4.6 g/day (TL2), 6.8 g/day (TL3), and 6.1 g/day (TL4). These values contrast to EPA's default values of 3.8 g/day (TL2), 8 g/day (TL3), and 5.7 g/day (TL4).

2.2.3 Adjustments Based on Modifications to the Default Relative Source Contribution

Consumption studies may also have information about how much marine fish is eaten by the population to be protected. Information about consumption of marine fish may lead to adjustments to the RSC component of the equation for calculating the fish tissue criterion. Because it is highly unlikely that concentration information will accompany the marine fish consumption data, the default concentrations for marine fish can be used in

combination with the site-specific marine fish consumption data to estimate methylmercury intake from marine fish (i.e., the RSC).

For example, the Lake Ontario study gives information about fish consumption from other sources. Although some of this consumption is from freshwater/estuarine sources, this consumption can be included in the RSC. The Lake Ontario study found that the mean consumption of non-sport fish by Lake Ontario fishers was 13 g/d. This value is essentially the same as the default value of 12.46 g/d, so no adjustment to the RSC is needed. A yearlong survey of licensed anglers in Michigan did find a lower value for consumption of non-sport fish than the default value (West et al 1993). This survey found a sport fish consumption of 14.5 g/d and non-sport consumption of 9.8 g/d. Absent data for a specific Michigan water body, the state can use the non-sport consumption data to adjust the criterion. There are no data sets for concentrations in non-sport fish consumed in Michigan, so the default value of 0.157 mg/kg, the species-weighted average methylmercury concentration in marine fish, is used and the following RSC is calculated.

$$RSC = FI_o \times C_o = \frac{9.8\frac{g}{d}}{70\,kg} \times 1.57 \times 10^{-4} \,\frac{mg}{g} = 2.2 \times 10^{-5} \,\frac{mg}{kg \cdot d}$$
(2-12)

where

 $FI_{o}$  = the marine fish consumption rate, and  $C_{o}$  = the marine fish concentration.

For a 70 kg adult, the RSC of 2.2  $\mu$ g/kg-d corresponds to an intake rate of 1.5  $\mu$ g/d. As the RfD for a 70 kg adult is 7  $\mu$ g/d, the local allocation, after RSC adjustment, would be 5.5  $\mu$ g/d using the subtraction method. This information is used with the Michigan sportfish consumption value of 14.5 g/d to calculate a fish tissue criterion:

$$TRC = \frac{BW \times (RfD - RSC)}{\sum_{i=2}^{4} FI_{i}} = \frac{70kg \times (10^{-4} \frac{mg}{kg \cdot d} - 2.2 \times 10^{-5} \frac{mg}{kgd})}{14.5 \frac{g}{d}} = \frac{5.5 \frac{\mu g}{d}}{14.5 \frac{g}{d}} = 0.38 \frac{mg}{kg}$$
(2-13)

The adjusted fish tissue criterion is higher primarily due to the adjustment for the sport fish consumption rate. If no adjustment had been made for the consumption rate of marine fish (i.e., the default RSC value of  $2.7 \times 10^{-5}$  mg/kg-d were used), the result would be a tissue criterion of 0.35 mg/kg. Although data show consumption of marine fish to be about 20% less than the default value, the corresponding adjustment to the criterion is only 0.03 mg/kg. The sensitivity of the criterion to the sport fish consumption value and the non-sport fish consumption value can be quantified by the partial derivatives of the criterion to each parameter. Using default values for all of the parameters shows the sensitivity of the default criterion to changes in sport-fish consumption value results in a larger change in fish tissue criterion than making the same adjustment to the non-sport fish consumption value. Thus, on a relative basis, the applicable fish tissue criterion is more sensitive to changes in sport fish consumption estimated by water body-

specific consumption data, and less sensitive to changes in estimated marine fish consumption.

$$\frac{\partial TRC}{\partial (\sum_{i=2}^{4} FI_{i})} = -\frac{BW \times (RfD - RSC)}{(\sum_{i=2}^{4} FI_{i})^{2}} \times = \frac{-5.11 \frac{mg}{d}}{(\sum_{i=2}^{4} FI_{i})^{2}} = \frac{-5.11 \frac{mg}{d}}{(17.5 \frac{g}{d})^{2}} = -1.7 \times 10^{-8} \frac{d}{g}$$
(2-14)

$$\frac{\partial TRC}{\partial (FI_o)} = -\frac{C_o}{(FI_o)} = \frac{kg}{17.5\frac{g}{d}} = -9.0 \times 10^{-9} \frac{d}{g}$$
(2-15)

#### 2.2.4 Body Weight and Other Exposure Factors

The RfD for methylmercury is in units of mass ingested per day per kg-body weight. Thus, the calculation of the fish tissue criterion based on the RfD requires assumptions about body weight. EPA recommends a body weight of 70 kg for adults (US EPA 2000a). This value is partially based on the third survey (NHANES III) conducted by the National Center for Health Statistics with participation from the CDC. NHANES III is a nationally representative study with a large sample size and is able to give the precise value of 75.6 kg for mean weight for adults (WESTAT 2000). Adding to the conservatism of the 70 kg value is that these data are now between 8 - 14 years old and average body weights may be trending upwards. The 70 kg value also is recommended for consistency with derivations of dose-response relationships. The EPA *Exposure Factors Handbook* (US EPA 1997b) advises that, for U.S. adults, a body weight of 71.8 kg is appropriate. This source encourages the use of values reflective of the population concerned, but cautions for the need to adjust the dose-response relationship, if the value is revised.

In a study of how eight states set fish advisories (Whipple 1999), it was noted that one state (Wisconsin) assumes that a nominal portion size is appropriate for a person of average weight, and that people above or below this average weight eat proportionally sized portions. This assumption results in a uniform methylmercury exposure to persons of different body weight from fish of a given concentration. Therefore, making site-specific adjustment to body weight without a corresponding site-specific adjustment to consumption may not be valid. In any case, changes to this parameter are unlikely to change as much as changes to other components of the criterion calculation, such as fish consumption, and have not been a focus of this study.

#### 2.2.5 Adjustments Based on BAFs and other Modeling

EPA decided to establish the recommended methylmercury water quality criterion as a fish tissue criterion instead of a water column criterion. This removes the BAF from the criterion equation. As a result, the fish tissue criterion cannot be adjusted based on site-specific or regional BAFs or other similar factors. EPA recommends a fish tissue criterion because fish tissue concentrations integrate the complexity of bioaccumulation, represent the human exposure route for methylmercury, are easier to measure than

water concentrations, are less variable with time than water concentrations, and are consistent with the fish advisory concept many states have adopted to address fish tissue levels.

In the TMDLs EPA Region 4 issued for waters in Georgia, the Agency established a water column criterion using BAFs calculated with site-specific or regional field data. However, based on the discussion of BAFs, especially the comments from peer reviewers on *Water Quality Criterion for the Protection of Human Health: Methylmercury* (US EPA 2001b), BAFs tend to be highly variable and less reliable than more direct measures of methylmercury concentration. The peer review comments are provided in Attachment A to the Appendix of the report. This issue is discussed more fully in Section 4.

#### 2.2.6 Adjustments Based on Toxicology

The site-specific adjustments discussed above are based on exposure. The fish tissue criterion is derived from exposure values based on fish consumption estimates coupled with the RfD, which represents methylmercury toxicity. Adjustments to the RfD certainly would change the criterion. EPA guidance allows for alternative toxicological values to be used when technical justification is provided. Other federal agencies have evaluated methylmercury risks and arrived at exposure guidance that differs from that of EPA. For example, in 1999, the Agency for Toxic Substances and Disease Registry published a Minimal Risk Level, equivalent to an RfD, for methylmercury of 0.3  $\mu$ g/kg-day based on the Seychelles study. This value is three times as high as EPA's RfD.

#### 2.2.7 Alternative Criteria Based on Biomarkers

Biomarker data such as blood or hair concentrations are direct indicators of how much users of a water body are exposed to methylmercury. These data are directly comparable with data used to establish the RfD (see Appendix A). Use of such biomarker information would remove or reduce many of the uncertainties associated with methylmercury consumption via fish consumption. In comparison to the use of biomarkers, a consumption-based estimate of methylmercury exposure requires estimates of the frequency of consumption of both self-caught and marine fish, estimates of the portion sizes, knowledge of the type of fish consumed, and an estimate of the methylmercury concentration typical of that species (or trophic level of fish) for the specific location. The collective effect of the uncertainties in each step of the above calculation can be large. Therefore, using biomarker concentrations instead of fish tissue concentrations as a criterion should be considered.

As with the derivation of the fish tissue concentration, biomarker concentrations should be set to a value consistent with the RfD in order to serve as a criterion. The hair concentration consistent with the RfD is 1.1 ppm according to the National Research Council report. The blood concentration associated with the RfD is 5.4 ppb when an adjustment is made for the difference in methylmercury concentrations observed in cord blood versus maternal blood (US EPA 2001a). These values for hair and blood concentrations provide possible alternative criteria. Barring any site-specific adjustment of the RfD, no site-specific adjustment of these values is necessary or possible. The
alternative criterion would only need to be compared with biomarker data from the population of concern for evaluating that population's exposure. Comparison with fish tissue concentrations would not be needed. In the National Research Council methylmercury report (Committee on the Toxicological Effects of Methylmercury, 2000), the relative merits of hair and cord blood as biomarkers are addressed. The advantage of cord blood is that it is a direct measure of the exposures to the developing brain of the fetus. However, cord blood is not an available biomarker for water body studies, but adult blood levels can be measured and used as an index of exposure. In comparison to cord blood, hair measurements are a less direct measure of the exposure to the organ of concern and include potential additional variability as an exposure measure. In contrast, hair can provide a better measure of average exposure over a period of months, whereas blood concentrations are more strongly affected by recent exposures. Finally, the willingness of members of the public to provide blood samples and safety and licensing issues associated with collecting and storing blood may weigh in favor of hair sampling.

While a biomarker can be a reliable measure of whether the total methylmercury exposure to an individual or group is high or low relative to the level set by EPA in the RfD. biomarker data do not indicate the relative mix of different sources of exposure. That is, data on the methylmercury concentration in hair or blood may indicate that someone is receiving exposure at 80% or 120% of the RfD, but there is no way to determine, based on that measurement alone, how much of that exposure came from a particular water body. In addition, the use of biomarkers would not completely remove errors and uncertainties; those associated with the analysis of hair or blood would remain, and these are not necessarily trivial. A recent evaluation of commercial laboratories that measure mercury in hair (Seidel et al, 2001) found the analyses to be unreliable. In EPA's guidance document on fish sampling (US EPA 2000d), EPA indicates that the cost for analysis for total mercury ranges from \$45-\$60 (1999 dollars). The Environmental Medicine Department Laboratory at the University of Rochester, where the samples collected in the Seychelles study were analyzed, charges a fee of \$50 per sample for analysis of the methylmercury content of blood or hair. Frontier Geosciences of Seattle will analyze hair samples (but not blood) for total mercury for \$115 per sample and methylmercury for \$195 per sample.

## 2.3 Consumption Study Requirements

Fish consumption information is the basis for making site-specific adjustments to the fish tissue criterion. Because the only exposure pathway for methylmercury is fish ingestion, consumption data are necessary for estimating intake. As described in Sections 2.2.1 through 2.2.3, consumption data useful for the specification of a fish tissue criterion can include the total amount of freshwater/estuarine fish consumed, the distribution of consumption among types of fish, and the amount of marine fish consumed.

Consumption data can be obtained with a variety of approaches, including recalled information, diaries, and on-site creel censuses. EPA's *Guidance for Conducting Fish and Wildlife Consumption Surveys* (US EPA 1998b) gives instructions on choosing a survey method and designing a consumption study. Other manuals for conducting creel surveys include that published by the American Fisheries Society (Malvestuto 1983).

The many different components of calculating exposure based on fish consumption introduce uncertainties that are not associated with more direct measurements of exposure, such as biomarkers. The various approaches that are used to obtain consumption data each have different advantages and disadvantages. These relative advantages and disadvantages are described by EPA (US EPA 1998b). Also, site-specific consumption estimates may be combined with generic or default values. For example, consumption data may be available only for fish caught in the water body and not for marine fish also consumed. In this case, default values for the RSC typically are used. As a result, the estimate of the RSC may be less certain for this specific population than the estimate of freshwater/estuarine consumption.

## 2.3.1 Guidelines for Evaluating Information Gathering Opportunities

There are various quantities that can be measured on a site-specific basis, including site-specific information on total fish consumption, consumption by fish type or trophic level, and tissue concentration by fish species or trophic level. At the outset of evaluating exposures from a particular water body, consumption data will often not be available. Adjustments to the criterion are not possible without obtaining adequate consumption data. Following are some suggestions for deciding what information might be worthwhile pursuing when the default fish tissue criterion has been exceeded.

The fish tissue criterion calculation is most sensitive to the value used for freshwater/estuarine fish consumption. This data may be more easily obtained than other components of the criterion calculation, such as the distribution of consumption by trophic level and marine fish consumption. Collecting only data for the consumption amount for fish caught out of the water body of concern should be considered a minimum effort. When a decision to conduct a creel survey is made, it is ideal to seek to collect data on all three factors affecting the fish tissue criterion: the total freshwater/estuarine consumption rate, consumption information on the distribution of fish consumed by trophic level or species, and marine fish consumption. To be fully informative, the part of the survey addressing marine consumption should include questions about consumption frequency, portion size, and the type of fish consumed.

Once site-specific data are obtained, the criterion can be adjusted as detailed in Sections 2.1.1 through 2.1.3. For water bodies where data are obtained, the adjusted fish tissue criterion is based on EPA's first data preference. This fish tissue criterion can be used at similar water bodies in the state if those water bodies do not have sitespecific data. This extension of the adjusted criterion is based on the second data preference EPA recommends. If concentrations at one of these other water bodies are above the criterion, then site-specific data may need to be obtained at this water body as well.

## 2.3.2 Cost-effectiveness

A screening analysis of the cost of obtaining consumption data may be useful. Studies using different approaches have different costs. Diary, telephone, and mail surveys tend to be of lower cost than personal interviews and creel surveys (US EPA 1998b). The two year diary and mail survey of consumption at Lake Ontario cost \$83,085. The one-year mail and telephone survey of Michigan fishers cost about \$30,000. The 9-month

creel survey performed for the Altamaha River in Georgia in 2001 cost a total of \$40,000 (Harrison 2002). Each of these studies provided different types of information. The Lake Ontario study provided site-specific information about consumption of sport fish caught in the lake and consumption of non-sport fish. The Michigan study provided statewide information about consumption of sport fish and non-sport fish. The Georgia survey provided information about the trophic level breakouts but not of per capita consumption. Gathering information about all the factors that can result in a site-specific adjustment will likely be more expensive than projects of more limited scope. Factors to be considered in evaluating the cost-effectiveness of conducting a consumption survey include the size of the population consuming fish from the water body and the cost associated with controls that may be imposed, absent a refined exposure survey.

# 2.3.3 Temporal Consumption Data

In making adjustments to the fish tissue criterion based on site-specific data, temporal variations need to be taken into account. The quantity of fish consumed and trophic level, size, or species breakouts should reflect fish consumed on an annual basis, not just the subset of fish consumed in one season.

Such seasonal variability also could affect the results of fish sampling, as discussed in Section 3.5.1. In order to facilitate temporally representative fish sampling, consumption surveys should obtain information about when fish are consumed out of the water body. Especially important is information about different fish populations consumed at different times of the year. Some important sport fish, such as migrating salmon, can only be harvested by recreational fishers during a specific season.

# 2.3.4 Spatial Consumption Data

A consumption study that effectively targets a representative sample of the population that fish and consume from a water body will presumably also represent the spatial distribution of fishing in the water body. However, it is important that spatial information about fishing be collected in the course of the study to aid planning of fish sampling, as discussed in Section 3.5.2.

# 2.4 Regulatory Acceptance

EPA, state, and/or tribal approval of a petition to obtain and use site-specific exposure data should not be an issue. EPA encourages states to obtain any local information to update the criterion for a specific site.

## 2.5 Statistical Issues Associated with Adjustments to the Criterion

In *Guidance for Conducting Fish and Wildlife Consumption Surveys,* (US EPA 1998b), EPA states that "the reader is therefore advised to consult an experienced survey researcher and/or statistician during the sample selection stage to achieve adequate representations of the survey population." While it is beyond the scope of this document to define statistical analysis methods appropriate for making adjustments to the criterion, some general comments on statistical issues can be made. Adjustments to the criterion are based on estimating exposure rates of those populations that use a specific water body. As discussed in Section 2.1.3.2, using average values for consumption, and therefore exposure, is consistent with EPA's default values for protecting sport fishers and subsistence fishers.

In the case where site-specific or regional consumption data are available, a reasonable statistical test is to determine whether the new consumption estimates are significantly different from the default values, in order to make adjustments to the default intake values recommended by EPA. A possible statistical test is the t-test. The t-test assumes an underlying normal distribution. Since consumption data is often log-normal, a log-normal transformation may be necessary to use this statistical test. Use of a t-test is consistent with the data adequacy tests EPA outlines in the Methodology (US EPA 2000a).

One test that can be made is to evaluate whether site-specific consumption data are statistically different from the default values. When using site-specific information, the adjusted central tendency (usually the mean) values should be statistically significant at an a level of 0.05, the most common acceptable level according to EPA's *Guidance for Conducting Fish and Wildlife Consumption Surveys* (US EPA 1998b). For an alternative value for freshwater/estuarine adult consumption to be used, it should be statistically different from the default value of 17.5 g/d. Alternative breakouts of trophic levels also should be statistically different from the default value of a value whether the site-specific data are different from the 3.8/17.5 for Level 2, 8.0/17.5 for Level 3, and 5.7/17.5 for Level 4. Similarly, one can test whether an alternative value for marine fish consumption (to calculate the RSC) is statistically different from the default value of 12.46 g/d. If, for any of these consumption measures, the alternative value is not statistically different from the data needed to support an adjustment have not been provided, and an adjustment should not be made.

2.6 Summary and Recommendations for Site-Specific Adjustments

Ideally, the fish tissue criterion for a specific population group and water body would be based on the following information:

- The distribution of fish consumed from the specified water body by the population group to be protected, including knowledge of the mean, 90<sup>th</sup> and 95<sup>th</sup> percentiles of consumption;
- Information regarding the consumption rates, stratified by fish species and trophic level;
- Information regarding the consumption of fish from other sources, including other freshwater and estuarine fish and marine fish; and
- Information on the fish type and methylmercury concentration in the other fish sources for purposes of adjusting the RSC.

Information showing that the site-specific consumption rate is significantly different from 17.5 g/day would have the greatest effect on changing the default criterion of 0.3 mg/kg.

Regarding trophic level, where sampling has been largely focused on trophic level 4 fish and consumption is mainly of trophic level 2 and 3 fish, the current database would misrepresent the concentrations in fish as consumed and an adjustment may have a significant effect on the fish tissue criterion. This situation is likely where state agencies have focused fish sampling on species likely to have high levels of methylmercury. Finally, the RSC could affect the default criterion if information can be assembled to show that the population group of interest eats significantly more or less than 12.46 g/day of fish from other sources, or if the other fish is shown to have methylmercury concentrations significantly different from 0.157 mg/kg. This last situation could occur if significant amounts of fish low in methylmercury (e.g., farm-raised catfish, shrimp) were included in the RSC.

## 3.0 Determining When the Criterion has been Exceeded at a Site

#### 3.1 Site-Specific Data to Determine Whether the Criterion Has Been Exceeded

The fish tissue criterion is either the 0.3 mg/kg default criterion recommended by EPA or a different value derived by methods described in Section 2. (It was also suggested in Section 2 that a biomarker-based criterion could be used in place of a fish tissue criterion). Determining whether the criterion is exceeded requires sampling of mercury concentrations in fish tissue. An appropriate average of the concentration data is compared to the criterion to determine whether the criterion has been exceeded. The appropriate average uses weighting based on the types of fish consumed. EPA provides default values for the distribution of trophic level breakouts. Site-specific distributions also may be based on trophic level breakouts, but also can be based on species and/or size of the fish consumed.

## 3.1.1 Data on Methylmercury Concentrations In Fish

Sampling fish tissue for mercury concentrations is described in EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories Volume 1: Fish Sampling and Analysis* (US EPA 2000d). As the title suggests, the focus of the guidance is for use in fish advisories and not for comparison with fish tissue criteria, such as the one for methylmercury. The approach described with the goal of defining an appropriate set of fish advisories is different from one to determine whether a fish tissue criterion has been exceeded. For some chemical contaminants of concern regarding fish, e.g., PCBs and dioxin, the substance tends to concentrate in the fat, and the question of whether to sample the whole fish versus the portions usually consumed can be an issue. Because methylmercury tends to accumulate in the muscle, this is not an issue for methylmercury. The guidance is to sample the fillet.

One of the main concerns is that none of the test methods for measuring either total mercury or methylmercury in fish tissue (or methylmercury in water) have been validated based on an interlaboratory study conducted with ASTM or other related procedures. Although certain methods have been used for years by various entities, there is no way, short of a validation study, to assess their ability to yield substantially the same results consistently, regardless of the laboratory doing the testing.

Also, the fish tissue criterion is for methylmercury and not total mercury. However, analysis of methylmercury in fish tissue costs as much as three times the cost of a total mercury analysis. Thus, EPA recommends that states measure total mercury concentrations in fish tissue and make the conservative assumption that all mercury is present as methylmercury (US EPA 2000d). This may be appropriate for the purpose of establishing fish advisories. This assumption should be treated with caution in determining whether the criterion has been exceeded, however, because such a determination can have regulatory consequences, as described in Section 4. For bottom feeding fish near sites where a significant quantity of inorganic mercury may have entered the water body (e.g., from mining) the assumption that methylmercury can be reliably estimated by measuring total mercury may not be valid.

If the use of total mercury concentrations show that the criterion is not exceeded, the conservatism of using total mercury ensures methylmercury concentrations do not exceed the criterion. However, if total mercury concentrations result in weighted averages slightly above the criterion, analyzing for methylmercury concentrations may show the criterion is not exceeded. In this case, the additional cost of methylmercury analysis may be justified, even if the purpose is to analyze sub-samples of all fish species and/or size groups. The *Guidance for Assessing Chemical Contaminant Data* document does contain applicable guidance for field and laboratory procedures and should be consulted on those matters.

# 3.1.2 Data on Methylmercury Distribution by Trophic Level

Concentrations for fish should be weighted by fish type consumed in order to reflect the actual exposures of the fish-consuming population. However, it is well established that methylmercury concentrations vary significantly depending on fish type or trophic level. A criterion determined by site-specific data may include such a distribution by trophic level, species, fish size, or a combination thereof. Absent such a site-specific definition of consumption distribution, the default values provided by EPA are used. In any case, fish of each type defined in the distribution should be sampled to allow determination of a weighted-average. This method and approach contrasts with sampling for fish advisories, where EPA recommends sampling one target species among bottom feeders and one target species among predators. If either species has concentrations over the screening level, development of fish advisories is undertaken (US EPA 2000d).

The procedure by which one determines the average methylmercury concentration for fish of a given trophic level is not specified clearly in EPA guidance. Ideally, one would use the concentrations for each fish of a given trophic level, weighted in proportion to the consumption rate of each species. Care should be taken when working from existing data on fish from a particular water body to understand whether and to what extent the samples are biased to over-represent locations of concern (such as near known point sources) or species of concern (such as top predators).

An example of how to make the weighted average calculation is provided using concentration data from Lake Whatcom, near Bellingham, WA, where there was a comprehensive study of fish tissue mercury concentrations in the lake (Serdar 2001). Because only seven data points regarding fish consumption are available for this lake, (Washington Department of Health 2001), default values for consumption provided by EPA are used. The mean mercury concentrations in edible muscle of Lake Whatcom fish collected and analyzed during 2000 are as follows:

Species	Trophic Level	Number of Samples	Mean Concentration (mg/kg)
Cutthroat Trout	3	30	0.07
Kokanee	3	30	0.12
Yellow Perch	3	30	0.19
Smallmouth Bass	4	95	0.45
Pumpkinseed	3	30	0.13
Brown bullhead	3	13	0.39
Signal crayfish	2	45	0.07

These measured concentrations are used in conjunction with default values for the distribution of consumption by trophic level, and the weighted sum compared to the default 0.3 mg/kg criterion. All fish measured can be classified as trophic level 3 fish except for signal crayfish, which is trophic level 2, and Smallmouth bass, which is trophic level 4. The mean value for trophic level 3 fish is 0.15 mg/kg, when averaged on the basis of each fish caught. However, this averaging approach does not consider that the trophic level 3 fish in this sample are of different sizes, or that some may be consumed more or less frequently than is represented by the number of samples. Using the 0.15 mg/kg value as representative of trophic level 3 fish, the default concentration calculation is as follows:

$$C_{avg} = \frac{3.8 \times C_2 + 8.0 \times C_3 + 5.7 \times C_4}{17.5} = \frac{3.8 \times 0.07 \, ppm + 8.0 \times 0.15 \, ppm + 5.7 \times 0.45 \, ppm}{17.5} = 0.23 \, \frac{mg}{kg}$$
(3-1)

This weighted average of 0.23 mg/kg is lower than the criterion of 0.3 mg/kg, so the data show that the default criterion is not exceeded.

Fish sampling can provide data on the methylmercury concentrations for different fish types or trophic levels, and the average fish concentration can be calculated by weighting by the fish type consumed. The weighting method is described in Section 2.2.2. The weights can be adjusted to reflect the actual distribution of fish types consumed as revealed by creel surveys, if that information is available or can be obtained. In some cases, the default trophic level breakouts recommended by EPA may be appropriate.

Creel surveys should be designed to provide enough information about concentrations at different trophic levels or by species to make calculations using the following equation.

$$C_{avg} = \frac{\sum_{i=2}^{4} FI_{i}C_{i}}{\sum_{i=2}^{4} FI_{i}}$$
(3-2)

where

- i = Trophic level number for fish (i=2,3,4) Fl<sub>i</sub> = Fish consumption rate of fish of trophic level i
- C<sub>i</sub> = Concentration in fish of trophic level i.

If data are available based on different criteria such as species or size rather than trophic level, fish concentration data can be analyzed in the same way as for trophic level; that is, one can sum the consumption-weighted concentration of each species.

#### 3.2 State or Regional Data

In a region with many recreational water bodies, data may indicate that the methylmercury concentrations across water bodies with similar characteristics are similar. It may be practical, for small and infrequently used water bodies, to assume that the fish in those bodies have mercury concentrations equal to those of the same fish in nearby water bodies.

## 3.3 Statistical Treatment of Fish Methylmercury Data

In discussing statistical treatment of fish tissue concentration data, EPA generally refers to central tendency values as representative. This means that where the guidance gives a choice of mean versus upper bound, this choice applies to consumption data, not to concentration data.

Use of an arithmetic mean is consistent with the development of the fish tissue criterion. The mean value concentrations for freshwater/estuarine fish reported in the Mercury Study Report to Congress (US EPA 1997a), based on EPA's national study of chemical residues in fish (US EPA 1992) and on measurements reported by Bahnick, et. al. (Bahnick et. al. 1994), provide mean concentrations by species. Based on these values, EPA determined that freshwater/estuarine and marine fish are the major exposure pathways to methylmercury, and that other pathways such as drinking water did not need to be considered. In the derivation of the RSC, EPA used the species-weighted mean concentrations in marine fish, based on data reported by the National Marine Fisheries Service (NMFS) (US EPA 2001b). In addition, EPA's Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories Volume 1: Fish Sampling and Analysis endorses the use of mean concentration values for comparison with screening values for fish advisories (US EPA 2000d). This use of mean values also applies to comparison of data with the methylmercury criterion. The only difference is that comparison with screening values for fish advisories may be species specific, while the mean used for comparison with the fish tissue criterion must be consumption weighted. This consumption weighting is either based on site-specific adjustments or the default breakout by trophic level.

EPA acknowledges the appropriateness of using mean concentration values with its endorsement of using composite samples. The EPA Fish Advisory Guidance states, "the use of composite samples is often the most cost-effective method for estimating average tissue concentrations of analytes in target species populations to assess chronic human health risks" (US EPA 2000d). Using upper-end estimates of concentrations in individual fish is necessary for the evaluation of acute health risks, which is not the case for methylmercury in fish. With this guidance, EPA recognizes that people who eat fish frequently, such as sport fishers and subsistence fishers, will, on average, experience the mean methylmercury concentrations of the fish. This will be true even if the contaminant levels in fish are distributed log-normally. For such a distribution, the geometric mean may serve as a more representative measure of central tendency than an arithmetic mean, but average exposures are best-calculated using arithmetic means.

3.4 Data on Mercury Concentrations in the Water Column or Sediment

Because the relation between the methylmercury concentration in fish and that in the water column is highly variable, the use of water column data should be discouraged. In order to compare these concentrations to the fish tissue criterion, some modeling of bioaccumulation, be it through the use of BAFs or other methods, is required. The high level of uncertainty in such assessments, as discussed in Section 4, makes this a poor choice for determining whether the fish tissue criterion has been exceeded.

## 3.5 Sources of Local Variability

Concentration data should be as representative of fish consumed from a water body as possible. Sampling of fish tissue should account for potentially significant temporal and spatial variability.

## 3.5.1 Temporal Variability

Fish tissue concentrations for many species may change seasonally. For determining the need for fish advisories, EPA recommends sampling from the late summer to early fall when lipid content of many freshwater species is at its peak (US EPA 2000d). This biases concentrations to be high for fat-soluble pollutants such as PCBs and dioxin, but is not true generally for methylmercury in muscle. For the purpose of comparison with the methylmercury fish tissue criterion, sampling times should be representative of when fish are caught for consumption from the water body. EPA also recommends avoiding spawning periods for fish tissue sampling (US EPA 2000d), which is appropriate unless consumption only occurs during spawning.

Data indicate that larger fish of a given species usually have higher methylmercury concentrations than smaller fish of the same species in the same lake or river. This suggests that methylmercury concentration in any given fish tend to increase with age. However, the mix of fish populations in a water body may change over time.

If consumption data show that the types of fish caught vary seasonally, fish tissue concentrations should not be restricted to fish consumed in one season. If fish are migratory, restricting sampling to one season may miss fish that make up an important part of the consumers' diet. In these cases, determining compliance with the fish tissue criterion requires concentration data from fish in all seasons when fish are caught and consumed from a water body. However, if only the quantity of fish caught and consumed varies, sampling does not have to be as temporally dependent.

## 3.5.2 Spatial Variability

Fish tissue concentrations may vary widely depending on the location sampled in the water body. The Lake Whatcom concentration data (Serdar 2001) show this possibility. Smallmouth bass have higher concentrations in basin 3 of the lake than the other two basins. Fish concentrations used for determining whether or not the fish tissue criterion has been exceeded need to represent locations where fish are caught for consumption. 3.5.2.1 Where Location May Affect Methylmercury Concentrations

For those water bodies with significant mercury point sources, the methylmercury concentrations in fish may vary with location within the water body. However, the factors that contribute to conversion of inorganic mercury to methylmercury and accumulation in fish are complex, and it is not always the case that a point source will lead to locally higher tissue concentrations. Fish sampled in locations with mercury point sources should be included in the average concentration if fishing occurs in these areas, but not included if the area near the point source is not used for fishing.

## 3.5.2.2 Where Methylmercury Concentrations Are Indirectly Affected

As noted in Section 3.5.2, the concentrations of methylmercury in a given species may vary with location. In addition, the location in a water body may affect the size and type of fish that are caught. If fish are only sampled where the largest fish or the species or trophic level fish with the highest methylmercury concentrations reside, a calculated concentration may not be representative of the mix of fish consumed from a water body.

# 3.5.3 Sampling Strategies to Address Temporal and Spatial Variability

For some water bodies, data on the concentration of methylmercury in fish may be available for a period of time and at a variety of locations. If such information is available (e.g., regarding the section of a stream and the date from which a particular fish was collected), the data can be examined for associations between the date or season when a fish was collected and the methylmercury concentration in the fish, taking species and size into account. Similarly, spatial associations in the tissue concentrations can be evaluated. For locations where the data indicate the locations and/or seasonal patterns are important to fish concentrations, site-specific consumption information should guide when and where fish sampling takes place. The information does not have to be extremely precise; sampling should be of fish that are representative of the species mix, locations and season where a representative member of the population of concern catches fish. One way to do this is to include questions in a creel survey regarding the locations where fish are caught, and to use this information in interpreting fish tissue data.

## 3.6 Statistical Issues Associated with Determining Compliance with the Criterion

Provided that statistical considerations were appropriately incorporated into the adjustments to the criterion, the statistical issues associated with collection and analysis of fish tissue data may be straightforward. This is because it is appropriate to use mean values of methylmercury concentrations, weighted by species or trophic level, for purposes of determining whether concentrations exceed the criterion. Two issues appear to be particularly relevant to this analysis.

First, there is the treatment of data reported as "less than" the method detection limit (i.e., nondetects). The convention recommended by EPA is to use one-half of the method detection limit for "less than" data in calculating mean values (US EPA 2000d). The rationale is that, where several samples are above the detection limit, it is reasonable to assume that a few below the detection limit probably contain some

mercury, notwithstanding the test result. That assumption probably is acceptable, provided that the detection limit is below the fish tissue criterion by a factor of 3 or more. In the rare case where the criterion is exceeded and there is a significant number of "less than" data, a more careful analysis is called for because the use of one-half of the detection limit typically overestimates concentration, especially for data that are log-normally distributed. EPA also recommends that measurements between the method detection limit and the method quantitation limit be assigned a value of the detection limit plus one-half the difference between the detection limit and quantitation limit (US EPA 2000d). That approach is inappropriate because it is based on the incorrect premise that a measurement greater than the detection level is equal to at least the detection level concentration. The appropriate value to use for measurements that fall between the detection and quantitation levels is that reported by the laboratory as it is the best available estimate of the true concentration. This value, however, is a **very noisy** measurement value (signal to noise ratio) that should be reported with an error band and used only with caution in comparison or computation.<sup>5</sup>

One simple screening approach is to calculate the mean concentration using both the detection limit and zero concentration for the "less than data. If the results from these two calculations, when weighted by trophic level, are both on the same side of 0.3 mg/kg, a more refined treatment of "less than" data will not make a difference in determining whether the criterion is met. However, if the weighted concentration is below 0.3 mg/kg when "less than" data are treated as zero concentration and above 0.3 mg/kg when they are included at the detection limit, then the actual result is indeterminate. For such a situation, one might fit a probability density function (e.g. lognormal, 1- or 2-parameter gamma, 2-parameter beta) to a frequency histogram of the fish concentration data, taking into consideration the mass of probability of the "less than" data (Yevjevich 1972)6. Once the fitted distribution parameters are known, the geometric mean or other measure of central tendency can be calculated and compared to the criterion. Other techniques, such as that described by Shumway et al. (1989),7 are also available. These techniques skirts the issue of assigning a single value to the "less than" data, assuming that they take on a range of values between zero and the detection limit as defined by the probability density function. While this approach is not entirely without bias in the statistical sense (except asymptotically as the sample size increases), it introduces far less bias than making simplistic guesses about what values "less than" data might represent.

An alternative approach to address the issue of "less than" data is to maintain frozen samples of fish tissue and, for analyses resulting in "less than" data, repeat the analyses using different laboratories or more sensitive methods. The available evidence, although requiring some interpretation, indicates that the most sensitive method now available (cold vapor spectrophotometry) has detection and quantitation levels of 0.521 and 2 ng/g, respectively (where 1 ng/g equals 1 ppb). These levels are well below the 0.3 ppm criterion. These values are reported in EPA's National Fish Tissue Study (described online at <a href="http://www.epa.gov/waterscience/fishstudy/tissue.htm">http://www.epa.gov/waterscience/fishstudy/tissue.htm</a>), the most recent and,

<sup>&</sup>lt;sup>5</sup> Gibbons, R.D. and Coleman, D.E. 2001. Statistical Methods for Detection and Quantification of Environmental Contamination.

<sup>&</sup>lt;sup>6</sup> Yevjevich, V. 1972. Probability and Statistics in Hydrology. Water Resources Publications. Littleton, CO.

<sup>&</sup>lt;sup>7</sup> Shumway, P. H., A. S. Azari, and P. Johnson. 1989. Estimating Mean Concentrations Under Transformation for Environmental Data With Detection Limits. Technometrics 31(3):347-356.

apparently, most reliable source of information on the performance of this method.<sup>8</sup> If mercury in fish tissue can be measured down to 2 ng/g (0.002 ppm), "less than" data are not likely to affect a determination of whether the mercury in fish exceeds 0.3 ppm.

3.7 Summary of Findings Regarding Determination of Whether the Criterion Has Been Exceeded

The two main factors that determine whether the methylmercury exposures to a population consuming fish from a lake or river are excessive are the consumption rates of fish of various species or trophic levels and the methylmercury concentrations of those fish. Depending on the data available, one can use all site-specific data or a mixture of site-specific data and default values to calculate a site-specific fish tissue criterion. The method by which one can adjust the fish tissue concentration, based on site-specific data on consumption, was described in Section 2. Given such a criterion, either adjusted for consumption data or based on EPA's default values, one can analyze site-specific fish tissue data to determine whether the criterion is met.

As a final comment regarding consumption surveys and fish sampling, it appears that the appropriate mix of fish tissue sampling and collection of consumption information is something that may best be worked out through an iterative process. That is, initial fish sampling may indicate whether the concentrations are well below, near, or substantially above the default criterion. If concentrations exceed the criterion based on trophic averaging using the default consumption distribution, more data can be collected to assess local consumption patterns (including data on both the type or trophic level and quantity of fish consumed) to adjust the criterion as described in Section 2, and to evaluate whether the criterion has been exceeded based on the revised criterion.

<sup>&</sup>lt;sup>8</sup> These values vary from the detection and quantitation levels EPA has published in its "Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories," Volume 1 (US EPA 2000d), which says that cold vapor atomic absorption spectrophotometry is the recommended analytical method for measuring mercury in fish tissue. That guidance reports that the range of detection limits for mercury using this method falls between 1.3 and 100 ppb, with quantitation limits between 2 and 10 ppb. The apparent anomaly (evident from fact that the range of the reported method detection level is far wider, and goes much higher, than the reported quantitation level) apparently is attributable to EPA's having derived that range from data for several different methods, rather than for cold vapor spectrophotometry alone. Thus, the detection and quantitation values reported in the Fish Tissue Study appear to provide more reliable information.

# 4.0 Criterion Implementation through the Regulatory Process

The intent of this section is to discuss the regulatory implications that arise when the applicable methylmercury fish tissue criterion has been exceeded. Thus far, actual experience in this area is limited primarily to EPA's approaches in the TMDLs prepared for water bodies in Georgia. States are expected to adopt their own implementation plans and policies when a fish tissue-based criterion is adopted into their state water quality standards. The approach assumed and overviewed here generally follows EPA's current practices, which currently are undergoing review. This section begins with an overview of the regulatory process, starting with a discussion of criterion development, and ending with the development of permit conditions.

Following the regulatory overview, issues associated with the use of the criterion in fish tissue in the context of the TMDL process, the development of load allocations, and the development of specific permit conditions or limits for point source dischargers is discussed. The state-of-the-science with regard to mercury and its implications for the regulatory process are reviewed. Particular emphasis has been given to mercury methylation, bioaccumulation, and watershed modeling. Following the review of each of these topics, knowledge gaps and the implications of these gaps for the regulatory process are summarized. Finally, recommendations for improving the regulatory process are made, taking into account the current limitations of our knowledge of mercury science.

## 4.1 Overview of the Regulatory Process

The regulatory process consists of several steps. First, mercury criteria must be adopted at the state level. This may consist of a single criterion, protective of all uses, or multiple criteria applicable to specific uses, perhaps even to specific water bodies. The criterion is then used to judge whether uses of the water body are being protected. If the criterion is exceeded, the water body is placed on the state's § 303(d) list of impaired waters. Once listed, a TMDL may be required for the water body to bring it back into compliance with applicable water quality standards. This step *can* utilize the translation of the criterion (if adopted as recommended by EPA as a fish tissue-based standard) to a water column-based standard.

Because of the ubiquitous nature of mercury in the environment, loadings to the water body may come from a variety of sources including atmospheric deposition, nonpoint watershed sources (including natural and older anthropogenic sources), and point sources. In order for allocation of load reductions to be scientifically and legally defensible, these various loads to the water body must be quantified with some degree of certainty; at least with enough certainty to establish that actions required of permittees are necessary, reasonable, and will contribute to the attainment of water quality standards in a desirable manner. The implementation of the TMDL may involve nonpoint source controls, including those already in place or planned for air emissions, and point source controls imposed via National Pollutant Discharge Elimination System (NPDES) permits. These steps are discussed in detail in the following sections.

#### 4.1.1 Development of Mercury Criteria at the State Level

The adoption of mercury criteria by the States has been inconsistent, partly due to changing guidance at the national level. As a result, states have adopted a variety of criteria for mercury. In 1984, EPA established a CWA § 304(a) water column criterion for total mercury of 12 ng/L. This criterion initially was developed to be protective of aquatic life, although in the criteria development document (US EPA 1985), it clearly was derived to be protective of human health. The criterion was developed by dividing the Food and Drug Administration (FDA) action level of 1.0 mg/kg in fish tissue by the freshwater and saltwater bioconcentration factors (BCFs) from the studies reviewed in the criterion development document. The resulting criterion for freshwater was 12 ng/L of methylmercury and, for saltwater, 25 ng/L of methylmercury. The criterion was issued for total mercury in the water column because of the difficulty of measuring methylmercury. Furthermore, it was stated that by basing the standard on total mercury, an additional degree of protectiveness would likely result. Some states adopted the standard as "protective of all uses," since at the time it was recommended, it was among the lowest of the numerically available criteria. Because of this, there has been a great deal of debate as to whether the 12 ng/L criterion represents a human-health based standard and whether it can be used in lieu of the narrative language in most state water quality standards for the protection of human health. In the same document, EPA recommended chronic and acute criteria for the protection of freshwater aquatic life of 12 ng/L and 2,400 ng/L, respectively; and chronic and acute criteria for the protection of saltwater organisms of 25 ng/L and 2.100 ng/L.

In 1995, EPA published updates (US EPA 1995) to the chronic criterion for the protection of freshwater aquatic life that was considerably higher (908 ng/L), and an acute criterion that was lower (1,694 ng/L), than the previous values. As of 1997, EPA had changed the mercury criteria again.<sup>9</sup> The acute freshwater aquatic life criterion was set at 2,100 ng/L (the saltwater value from 1985) and the acute criterion for saltwater species was set at 1,800 ng/L. The chronic criteria for protection of freshwater and marine species remained at 12 ng/L and 25 ng/L, respectively. In the same document, EPA published a risk-based level of 140 ng/L for combined consumption of water and organisms and 150 ng/L for consumption of organisms only. This criterion of 150 ng/L was adopted by a number of states, including South Carolina, for the protection of human health.

In December 1998,<sup>10</sup> EPA changed the criteria for mercury again. The freshwater acute criterion was set at 1,400 ng/L (down from 2,100 ng/L), and the freshwater chronic criterion was set at 770 ng/L (up from 12 ng/L). The saltwater chronic criterion was changed to 940 ng/L (from the previous criterion of 25 ng/L). The human health criteria also changed dramatically. The level set for consumption of water and organisms went to 50 ng/L (from the previous 140 ng/L) and the criterion for organism consumption only was set at 51 ng/L (from the previous 150 ng/L). These values remained the same until EPA published corrections to its § 304(a) criteria in April of 1999 (US EPA 1999).

The State of Washington uses a value derived from the National Toxics Rule (NTR) for § 303(d) listing, as it does not have its own promulgated human health regulatory standard. Its value of 0.825 ppm is derived using the NTR human health criterion based

<sup>&</sup>lt;sup>9</sup> As reported in the Code of Federal Regulations 40 CFR § 131.36 (7-1-97 Edition)

<sup>&</sup>lt;sup>10</sup> 62 Fed. Reg. (Dec. 7, 1998) / Notices

on consumption of organisms only and converted to a fish tissue-based value using the bioconcentration factor for total mercury from the 1985 mercury water quality criteria document (Serdar, 2002, personal communication). Some states have separate values for water quality criteria, screening values used to list waters or to recommend waters for further evaluation of potential human health risks, and fish consumption advisories or guidelines. For instance, the State of California uses a screening value of 0.3 ppm in fish, but has separate triggers for issuing fish consumption advisories (California EPA, 2001).

The lack of clarity with regard to mercury criteria has led to confusion and inefficiencies, as in the case of the State of Georgia. In 1998, when Georgia sent its list of impaired waters to EPA Region 4 for approval, the standard was 12 ng/L, which had been adopted as protective of all uses. The State also had a narrative toxics standard, but there was no numerical basis for placing waters on the § 303(d) list. EPA disapproved Georgia's proposed 1998 list and required that the State list those waters that had fish consumption guidelines posted due to mercury in fish tissue. The rationale was that if conditions were such that the public's full and unrestricted use of the resource was limited, then the water must be impaired. While State officials argued that their riskbased fish consumption guidelines were for informational purposes only and did not constitute an advisory of restricted use, this public information tool came to have the force of a regulation. Nearly one hundred water bodies were placed on Georgia's 1998 § 303(d) list as impaired due to mercury in fish tissue, even though there was never any documentation of exceedance of the 12 ng/L mercury standard in water, which was adopted as protective of all uses. The threshold for listing was 0.23 mg/kg, the guidance for limiting consumption to one meal per week.

Subsequently, TMDLs were required by court order for listed waters. A mercury TMDL for the Savannah River initially was proposed by EPA Region 4 in February 2000. Due to the volume of comments received, EPA collected data in the summer of 2000 and reproposed the TMDL in December 2000. Meanwhile, additional data were collected on six South Georgia Rivers for which TMDLs were proposed in August 2000. In January 2001, EPA published its new methylmercury criterion. Following an additional comment period, the Savannah River TMDL was finalized in February 2001, which did not utilize EPA's new methylmercury criterion. In August 2001, the six South Georgia TMDLs were reproposed, along with new TMDLs for middle Georgia rivers, which *did* make use of the new methylmercury criterion. As a result, many of the listed rivers were shown not to be impaired and load reductions were not required by the TMDLs. Subsequent to this, in Fall 2001, the Georgia Environmental Protection Division informally adopted EPA's methylmercury criterion of 0.3 ppm and a detailed protocol for listing waters, divorced from its fish consumption guidance protocols. Due to this action, many of the waters originally listed in 1998 were proposed for removal from the 2002 list, including the Savannah River segments.

Although EPA's publication of a methylmercury criterion seems to be a step in the right direction, it appears to have had the effect of increasing the confusion in the regulatory process at the state level. The first step in the process for states that do not have a human health criterion for mercury may be to adopt the new criterion as an interpretation of narrative toxics language. In some cases, it may be adopted to replace an existing human health numerical standard. However, its adoption may lead to a situation where dual standards (i.e. a fish tissue standard and a water column standard) exist. In addition, the translation of the fish tissue-based standard to a water column criterion for

the purpose of establishing TMDLs may lead to multiple water quality standards in certain water bodies. It is critical that EPA's forthcoming implementation guidance recognize and address these possibilities. At this time, the process by which states will adopt and implement the new methylmercury standard is very unclear.

## 4.1.2 303(d) Listing of Water bodies

Listing of water bodies also has been very inconsistent from state to state. A number of states continue to make use of the FDA guideline of 1 mg/kg in fish tissue for listing water bodies. A number of other states have adopted their own risk-based guidelines or advisories for listing purposes. Some, like the State of Washington, have derived criteria based on recommendations in the National Toxics Rule for the protection of human health. Yet other states have made blanket listing of all water bodies or of entire watersheds. This disparity leads to some untenable situations where interstate waters are involved when listings eventually lead to the establishment of TMDLs. For instance, in the case of the Savannah River mercury TMDL, EPA concluded that the appropriate water quality criterion for Georgia's part of the river was 2.8 ng/L, while South Carolina could continue to use a standard of 150 ng/L. In fact, because the TMDL was court-mandated only in Georgia (not in South Carolina), the TMDL was only applicable to Georgia dischargers. EPA's guidance on the implementation of its methylmercury criterion should recognize the difficulties that ensue from inconsistent adoption and application of standards relevant to listing.

Following the confusion that developed around the use of fish tissue advisories for placing water bodies on state § 303(d) lists after EPA Region 4 published its first TMDL proposal for the Savannah River, EPA's Office of Water published, on October 24, 2000, a document entitled "Guidance: Use of Fish and Shellfish Advisories and Classifications in 303(d) and 305(b) Listing Decisions" (US EPA 2000e). That document was very general and it will need considerable clarification in the Agency's implementation guidance.

# 4.1.3 Development of TMDLs

TMDLs generally must be established where water bodies have been placed on a  $\S$  303(d) list due to excursions of water quality standards attributed to pollutants. In the case of mercury, the establishment of TMDLs is a particularly difficult and controversial issue.

Mercury TMDLs have been established for only a few water bodies in the United States and are underway in a few others. Where they have been proposed or established, two issues seem to arise consistently. First, EPA has tended not to develop TMDLs based on achieving the fish tissue criterion directly, using instead a conversion to a water column value. Second, EPA has been unable to reliably ascertain the mercury loading sources and amounts that are needed to develop a valid TMDL. Both are discussed below.

#### 4.1.3.1 Development of a Water Column Criterion from a Fish Tissue Criterion

EPA finalized its methodology for deriving ambient water quality criteria for the protection of human health in October, 2000 (US EPA 2000a). The methodology uses the following formula to calculate a water column value reportedly protective for bioaccumulative pollutants. That value is referred to as the "water quality target" (WQT) and is defined by the following equation:

$$WQT = \frac{(RfD) \times (BW) \times (CF)}{(FCR) \times (BAF) \times f(MeHg)}$$
(4-1a)

where

WQT = the water quality target (ng/L) RfD = the reference dose (mg/kg-day) BW = the receptor body weight (kg) CF = a units conversion factor (10\*6 ng/mg) FCR = the fish consumption rate (kg/day) BAF = the bioaccumulation factor (L/kg), and f(MeHg) = the ratio of methyl to total mercury (dimensionless).

There are a number of issues associated with this computation. First, note that the equation uses the RfD, not the fish tissue criterion, to calculate the WQT. In other words, the formula does not provide a direct means of translating EPA's fish tissue criterion into a water column criterion. In order for this calculation to be consistent with the 0.3 ppm fish tissue criterion, the fish consumption rate must match the Agency's assumption of 17.5 g/day and the RfD must be reduced by the RSC for the consumption of marine fish.

The second issue is that this simplistic equation assumes a constant proportionality between fish tissue concentration, water column methylmercury, and water column total mercury, a questionable assumption that has immense implications in the regulatory process. Yet this important assumption underpins the Agency's current approach to regulating mercury in water. Even the most refined models available for mercury TMDL development have linear formulations (i.e., the algorithms assume that fate and transport processes depend on the concentration of total or methylmercury in the aquatic system) and, as a result, tend to give linear predictions of the relationship between fish tissue levels, water column concentrations, and mercury loadings or load reductions to water bodies. This leads to statements such as "in order to bring fish tissue concentrations below 'x' parts per million, water column concentrations must be brought to 'y' parts per trillion or lower." Because the methylation and bioaccumulation processes in a given water body are formulated in a linear fashion with respect to total mercury, a linear relationship between total mercury and fish tissue concentrations is presupposed; a speculative assumption at best. Indeed, most evidence suggests that there is little correlation between total mercury in a water body and mercury concentrations in fish (e.g., Gilmour et al 1991,1998; Cope et al 1990; Krabbenhoft et al 1999; Kelly et al 1995; Monson and Brezonik 1998).

## 4.1.3.2 Development of Current Load Estimates

The development of current loading estimates also is fraught with uncertainty. There is considerable uncertainty in atmospheric deposition rates unless they are site-specifically measured, primarily due to the potential influence of local sources. However, there is perhaps even greater uncertainty as to how much mercury is retained in terrestrial systems and re-emitted back to the atmosphere. Therefore, the quantity of mercury that is transported from watersheds to aquatic water bodies cannot be quantified with reasonable confidence. The model primarily being used by EPA or the states to model this process is Watershed Characterization System (WCS) (US EPA 2001c). Unfortunately, this model has not been calibrated or verified with actual data, and due to the questionable results its previous applications have generated, its validity is questionable.

Another considerable source of uncertainty is that component of the nonpoint source mercury load from the watershed to the water body consisting of naturally-derived mercury (i.e., mercury from weathering of watershed soils and rocks) and older ("legacy") anthropogenic mercury; mercury deposited from natural sources (i.e., volcanoes, forest fires) or older industrial sources (i.e., smelters, incinerators) that are no longer amenable to control except through management practices of unknown efficacy. Where point sources are known to contribute more than a *de minimis* amount of mercury to the water body, the nonpoint loads must be quantified in order to put the load from point sources, and the degree to which they require controls, into perspective.

## 4.1.4 Implementation of TMDLs

Implementation of mercury TMDLs requires states to specify reductions in loads to achieve water quality criteria, where feasible. Once these load reductions are specified, they must be allocated by some rational process to the known sources. Traditionally, load reductions for point sources are implemented and verified through the development of permit limits and monitoring requirements for dischargers. Some of the major issues with the existing regulatory approach are identified below.

## 4.1.4.1 Development of Load Allocations

The major issues with development of load reductions and subsequent allocations are the uncertainties associated with the magnitude of the loads. In many cases (e.g., all of the mercury TMDLs completed in Georgia), the point source contributions are so small as to not warrant imposition of a reduction. Furthermore, it may be very expensive for these minor sources to identify and control trace sources of mercury in their processes. Other major issues include accounting for mercury already present in process water intakes and requirements for municipalities or industries to treat mercury that may be present in storm water. It may be very difficult and expensive for facilities to identify and account for the increment of mercury discharged from their facility due to their activities, above those levels and loads in their intake water or naturally occurring in rainfall.

## 4.1.4.2 Development of Permit Limits

The development of permit limits for dischargers will depend on whether or not a TMDL and an implementation plan have been developed. Where that effort is complete, it will likely address the primary issues in the permitting process, such as the appropriate water quality standard, mixing zones, compliance schedules, and intake pollutants.

## 4.1.4.3 Time To Attainment

An ancillary, but related, issue that EPA's implementation guidance should address is the time required to bring water bodies back into attainment, if feasible. EPA should acknowledge that, where attainment is feasible, it may take decades or longer, due to the complexity of mercury fate and cycling in the global system. Otherwise, states will adopt "interim permitting" policies to apply prior to completion of the TMDL process. Given the long time periods assumed for mercury standard attainment and the need for a thorough technical analysis to support attainment decisions, EPA should not encourage states to impose mercury reduction burdens on point sources unless there is ample evidence that a particular point source is significantly contributing to the water quality standard excursion.

## 4.2 Scientific Issues in Regulatory Process

Nearly all mercury released by point and non-point sources to the environment (via air, water and solid waste) is in the form of inorganic mercury, whereas most of the mercury in fish tissue is in the form of methylmercury. Therefore, if EPA wishes to translate the fish tissue methylmercury criterion into a water column criterion, a relationship between total mercury and methylmercury and a clear understanding of the processes that contribute to mercury methylation and its bioaccumulation in fish are required. In this section, we review these key elements of mercury science and discuss knowledge gaps.

## 4.2.1 Mercury Methylation Process

Methylation of mercury in the environment is an important link between total mercury in the environment, its availability to fish, and ultimately its toxicity to humans and wildlife. Mercury methylation is influenced by a number of complex environmental parameters, and no adequate predictive tools or models currently are available to predict methylation rates in the environment. The factors that affect methylation, scientific knowledge gaps on methylation, and implications of those knowledge gaps on developing numeric criterion for mercury are reviewed below.

## 4.2.1.1 Mercury Methylation in the Environment

Ullrich et al (2001) provide a comprehensive and up-to-date review of factors affecting methylation in the aquatic environment, and a large portion of information in this section is taken from this reference. The chemical form (speciation) of mercury in aquatic systems is strongly controlled by pH, redox (Eh), and microbial population, as well as by

the concentrations of inorganic and organic complexing agents (ligands). In most freshwaters, the predominant form of mercury is ionic mercury in the divalent state (Hg(II)); whereas in fish, more than 90% of mercury is in the form of methylmercury (CH<sub>3</sub>Hg, monomethylmercury). Thus, methylation of ionic mercury to methylmercury is an important process that determines the bioaccumulation of mercury in fish.

It also is important to note that demethylation, which is kinetically favored in aerobic systems, is an important process. In fact, in some waters net demethylation occurs. The net result of the methylation and demethylation processes is of greatest concern at the watershed level.

Monomethylmercury is the most ubiquitous organomercury compound in freshwater and estuarine systems; whereas dimethylmercury is the dominant methylated species in deep ocean waters. The ratio of methyl to total mercury concentrations is usually higher in the water column than in sediments, and is higher in freshwater than in estuarine environments. In estuarine and marine waters, monomethylmercury is typically less than 5% of total mercury content. Up to 30% of total mercury in the water column of freshwater lakes and rivers can be found as methylmercury; however, it is normally on the order of a few percent.

The methylation of inorganic mercury in waters and sediments takes place in both remote and environments directly affected by human activities. Methylation occurs predominantly in sediments and to a lesser extent, in the water column. Maximum methylation rates usually occur at the redox boundary, which generally occurs at the sediment-water interface. The redox boundary varies seasonally and can influence the uptake of methylmercury by bottom-feeding organisms.

Mercury methylation can be microbially mediated or abiotic in nature, with the latter generally considered to be of minor importance. It has been shown that the transfer of methyl groups to Hg<sup>2+</sup> is a carbanion process, and methylcobalamin is thought to be the only natural methylating agent capable of transferring methyl groups as carbanions (Ridley et al 1977). Little is known about the biochemistry of methylmercury formation in the natural environment. The potential for microbial methylation generally is thought to be higher under anaerobic conditions, and sulfate-reducing bacteria have been identified as the principal methylators of inorganic mercury in anaerobic sediments (Compeau and Bartha 1985). As biological mercury methylation takes place within microorganisms, cellular uptake of mercury plays a key role in the methylation process.

Abiotic methylation can be mediated by humic substances, by transmethylation reactions between mercury and lead / tin alkyls used as gasoline additives, and by photochemical reactions or other processes. Humic substances may play an important, yet poorly understood role in both biological and non-biological methylation processes, as evidenced by large methylmercury production in wetlands, which tend to have high amounts of humic substances.

## 4.2.1.1.1 Factors Affecting Methylation

Formation of methylmercury in aquatic systems is influenced by a number of environmental factors. While the microbial activity and the concentration of bioavailable

mercury primarily determine methylation rates, parameters such as temperature, pH, redox potential, and the presence of inorganic and organic complexing agents play a complex, yet poorly understood, role in the methylation process.

*Microbial Activity*: It generally is believed that anaerobic sulfate-reducing bacteria are the principal methylators of inorganic mercury in both freshwater and estuarine environments (e.g., Gilmour et al 1992). Recent studies also indicate that these same bacteria also are capable of mediating methylmercury degradation. Not all sulfatereducing bacteria are capable of mercury methylation and methylation rates are not always correlated with sulfate concentration or with sulfate-reduction rates. The efficiency of microbial methylmercury production appears to depend chiefly on the activity and structure of the bacterial community, bioavailable mercury concentration, and the availability of nutrients and electron acceptors such as sulfate (Choi and Bartha 1994). According to Compeau and Bartha (1985), methylation potential of sulfatereducing bacteria is greatest when sulfate is limiting; and at high sulfate concentrations, sulfide produced in respiration may inhibit methylation through the formation of HgS precipitates or charged Hg-S complexes that are not readily bioavailable.

Sulfide: Several studies have reported that high sulfide concentrations inhibit methylmercury formation, and an inverse relationship between sulfide concentration and methylmercury production in sediments and pore waters also has been observed. On the other hand, increased methylmercury production also has been observed under certain sulfide concentrations (e.g., Craig and Moreton 1983). This suggests that, while high concentrations of sulfide can greatly reduce methylmercury production, it is not usually completely inhibited (Ullrich et al 2001). It is generally believed that the inhibitory effect of sulfide on methylation is due to the formation of insoluble HaS precipitates that are not bioavailable. However, high concentrations of dissolved mercury observed in sulfidic porewaters suggests that sulfide may actually help mobilize mercury through the formation of soluble mercury-sulfide complexes. Sulfide may also affect methylation through the formation of neutral HgS° species that can diffuse readily through cell membranes (Benoit et al 1999). On the other hand, formation of charged polysulfide complexes actually can decrease bioavailability, but its effect on methylation is not clear. As the primary pathway for methylation is by sulfate-reducing bacteria, more research is needed to identify the role of various sulfur species and other parameters on methylmercury formation.

*Temperature*: Several studies have indicated that maximum methylation activity occurs during mid- or late-summer (e.g., Watras et al 1995). Other studies have found higher methylmercury concentrations in spring than in summer (see AMEC 2001 or Section 4.2.2.2 below). While increased temperature can contribute to increased microbial activity, it also affects seasonal changes in productivity/nutrient supply, redox conditions, and demethylation rates.

*pH*: There has been concern that low pH values may lead to increase in the production and/or bioaccumulation of methylmercury because elevated mercury levels have been observed from fish in acidified lakes. Enhanced methylation has been observed in low pH waters and sediments; however this process is dependent on the redox state of the system (in anaerobic systems, acidic pH lowers methylmercury production) and other factors. pH may indirectly affect methylation by altering the mobility and partitioning of mercury and methylmercury in soils, stimulating methylmercury production through the addition of sulfate (in acid rain), and by changing microbial activity (particularly the

sulfate-reducing species) or cellular uptake of Hg<sup>2+</sup>. Changes in pH also can alter mercury speciation (e.g. enhanced production of elemental mercury, altering the binding of mercury to organic matter and other ligands), which in turn can affect the amount of ionic mercury available for microbial methylation. Demethylation rates are also pH sensitive, albeit to a lesser extent than methylation rates.

*Organic Matter*: The role of organic matter in methylation also is very complex and poorly understood. Observed increases in methylmercury concentrations with higher dissolved organic carbon (DOC) c oncentrations have been attributed to a stimulating effect of organic nutrients on microbial methylation activity (i.e., microbes utilizing organic matter as energy source when sulfate is limiting). Direct abiotic methylation of mercury by humic and fulvic acids (the refractory portions of dissolved organic matter) also could be very important, particularly in wetlands where high generation of methylmercury has been observed. This mechanism largely has been ignored and, to date, it is not clear to what extent abiotic methylation contributes to methylmercury production in organic-rich sediments and lake waters. It may be hypothesized that where organic matter is labile and readily biodegradable, it may promote methylation by stimulating microbial growth; and where the organic matter is recalcitrant and consists of high molecular weight humic and fulvic acids, it may contribute to abiotic methylation.

Decreased methylation has also been observed at high concentrations of organic matter in both natural systems as well as in experimental studies, and it has been suggested that dissolved organic carbon (DOC) may strongly bind with inorganic mercury at sulfurcontaining functional groups, rendering them unavailable for bacterial methylation. Even if methylmercury forms, it may be complexed by DOC and, therefore, not available for bioaccumulation. DOC also can compete with sulfide for mercury binding and favor the mobilization of mercury through the formation of Hg-DOC complexes. In mercury binding with DOC, pH may play an important role where protons compete with metal binding sites in organic matter. Humic substances, which are recalcitrant, highmolecular weight fractions of organic matter, also can reduce Hg<sup>2+</sup> to the volatile Hg<sup>o</sup> species, both directly as well as by enhancing the reduction rates in photochemical reactions, thus reducing the mercury burden available for methylation.

Redox Conditions: Even though mercury methylation occurs in both aerobic and anaerobic conditions in the natural environment, methylation rates are highest in anoxic sediments and waters, and the stability of methylmercury is greatest in anaerobic environments. This may be due to the reduced activity of sulfate-reducing bacteria under aerobic conditions and the enhanced degradation of methylmercury in aerobic conditions. It appears that anaerobic methylation is predominantly microbial in nature and, therefore, enhanced by the presence of organic matter; whereas abiotic methylation is favored under aerobic conditions and is suppressed by the presence of organic matter (possibly due to complexation with organic matter rendering mercury unavailable for methylation). Methylmercury concentrations usually are highest in the moderately anaerobic surface sediments (mostly at the oxic-anoxic interface) and rapidly decline with depth. Likewise, in stratified lakes and estuaries, methylmercury concentrations are usually highest at the oxic/anoxic boundary layer. Changes in redox conditions in water column and sediment layers also result in seasonal variations in methylmercury concentrations. Organic matter, nutrients, pH, and sulfides significantly influence the redox effects on methylmercury production.

*Salinity*: The methylating activity of marine and estuarine sediments is usually lower than that of freshwater sediments, partly due to salinity effects. The negative effect appears to be a result of formation of charged sulfide complexes (from sulfate in sea salt) in seawater and charged mercury-chloride complexes such as HgCl<sub>4</sub><sup>2-</sup> that limit the methylation process. Thus, estuarine fish tend to have lower methylmercury in their tissue than comparable species in freshwater fish (Gilmour and Riedel 2000).

In summary, mercury methylation is primarily a microbially mediated process, and the precise mechanism of methylmercury formation still is unclear. Mercury methylation and demethylation rates in aquatic systems are influenced by both the speciation and biochemical availability of mercury and by a large number of interrelated environmental variables, such as biological activity, nutrient availability, pH, temperature, redox potential, and inorganic and organic complexing agents. The importance of each of these parameters and their complex interactions varies across different ecosystems and even within the same type of water bodies. Different mechanisms of methylation may occur in sediments and in water. Seasonal variations in methylmercury production appear to be related to temperature, redox effects, seasonal changes in nutrient availability and mercury availability. Sulfur speciation and dissolved organic matter complexation are other important factors that are not well understood.

## 4.2.1.1.2 Knowledge Gaps

Despite the vast body of literature on the subject (348 publications cited in Ullrich et al 2001), we still are unable to predict mercury methylation rates or the likely effects of environmental perturbations on methylation processes in natural systems due to the complexity of the systems described above. Since laboratory studies look at simple systems with few variables at a time, it also is difficult to directly compare the results of the laboratory studies published to date with the processes and rates in the natural environment. Knowledge gaps exist in the following areas:

<u>Biotic vs. Abiotic Methylation</u>: While it widely is believed that mercury methylation is biologically mediated, review of literature by Ullrich et al (2001) suggest that there may be more than one mechanism of methylmercury formation. Abiotic methylation, particularly those mediated by humic substances, could be very important in wetlands and other ecosystems, but the significance of such processes in natural environments is unknown.

<u>Methylation vs. Demethylation</u>: A portion of methylmercury generated is demethylated by microorganisms, photochemical reactions and other processes. Sulfate-reducing bacteria, which were considered to be important methylating agents, also now are considered to be active demethylators. It is not clear what environmental conditions cause these microbes to carry out methylation vs. demethylation processes.

<u>Biomethylation</u>: Review of the literature suggests that methylation can be caused by sulfate-reducing bacteria, as well as a number of other types of bacteria that have not yet been identified. In the case of methylation by sulfate-reducing bacteria, the optimum sulfate concentrations required for methylation vary widely between different ecosystems and are difficult to predict. For example, bacteria in estuarine systems can methylate mercury at much higher sulfate concentrations than in freshwater systems. In addition, since bacteria that methylate mercury also are capable of demethylating, we are unable to predict biomethylation rates in natural systems.

<u>Role of Organic Matter</u>: Natural organic matter in soils, sediments, and water affect methylation in several ways. While natural organic matter can provide a stimulating effect on bacterial methylation in some systems, it may promote abiotic methylation in other systems, or inhibit mercury methylation (due to strong complexation) under other environmental conditions. The exact role of organic matter in a given system often is ignored in predicting methylation rates. Because of the complex structure and composition of organic matter and due to the paucity of thermodynamic data for organic matter - mercury complexes, the role of organic matter on the speciation and bioavailability of mercury has not been well described or modeled.

<u>Sulfur Chemistry</u>: Sulfur speciation is an important variable in methylation process. In addition to the role of sulfate on the methylation process, reduced sulfur can complex with mercury and form charged or uncharged mercury-sulfide complexes determining whether or not mercury becomes available to the microbes for methylation. Various stoichiometries of mercury-sulfide complexes have only been speculated, and competitive reactions between sulfide, organic matter, and mercury are not well defined.

Synergistic and Antagonistic Effects: From previous discussions it is apparent that each of the variables discussed above have multiple influences on the methylation and demethylation process. For example, low concentrations of sulfate can limit microbial methylation, while high concentrations of sulfate can result in the formation of excess sulfide concentrations that complex with mercury and inhibit mercury methylation. Some of the above parameters can alter the effect of other influencing factors on mercury methylation. For example, pH and redox can affect directly methylation and bioaccumulation, as well as alter mercury speciation, sulfur chemistry, and microbial activity. Due to the complex role of any one of the above parameters on methylation, it is difficult to predict their combined effect in natural systems with existing models.

There are many factors affecting methylation, but the current science is not adequate to resolve which factors are most important and allow models to move towards a more predictive capability. Research into factors affecting methylation is ongoing, however, with significant progress expected over the next several years.

<u>METAALICUS Project</u>: Some of the questions on the rates and factors governing mercury methylation may be answered by the METAALICUS Project (Mercury Experiment to Assess Atmospheric Loading in Canada and the United States) currently underway at the Experimental Lakes Area (ELA) in northwestern Ontario, Canada (Harris et al 2001). METAALICUS is a multi-disciplinary whole-ecosystem experiment in which stable, non-radioactive, isotopes of inorganic mercury (Hg(II)) are added to the upland, wetland and the lake surface to determine the relationship between atmospheric mercury loading and fish mercury concentrations. One of the goals is to determine how much of the newly deposited atmospheric mercury becomes bioavailable for methylation and biological uptake.

4.2.1.1.3 Implications of Knowledge Gaps

Any efforts to reduce methylmercury concentration in fish tissue require a clear understanding of the processes that produce methylmercury and factors that promote demethylation. Methylmercury production in aquatic systems is not a simple function of total mercury concentration in the system (see discussion below). Rather, as discussed above, it is affected by a number of complex, inter-related factors, which may result in a non-linear relationship between total and methylmercury. Since any or all of these (or other) parameters can control methylation, either alone or in a complex interrelated process, ecosystems respond differently to changes in these parameters and, at present, there is no simple way to predict methylation rates in natural environments. In the Florida Everglades, for example, contrary to conventional wisdom, the percentage methylmercury increases from north to south, opposite the gradients in nutrient, sulfate and sulfide concentrations (Gilmour et al 1998). Regulatory measures, such as reducing mercury loading rates from atmospheric or point sources, will be less successful in reducing mercury levels in fish without further understanding of these complex processes.

## 4.2.1.2 Use of Total Mercury as a Regulatory Tool

Nearly all mercury released by point and non-point sources to the environment is in the form of inorganic mercury; whereas most of the mercury in fish tissue is in the form of methylmercury. To date, EPA's approach to translating fish tissue methylmercury concentrations into water column total mercury values has assumed that the quantity of methylmercury in the water column is proportional to the amount of total mercury in the water column. In most natural environments, however, methylmercury production is rarely a constant value nor a function of total mercury concentrations in the water column alone. Given that demethylation also occurs, with an attendant set of environmental factors that affect it, it is not surprising that the resultant levels of methylmercury are not proportional to total mercury in aquatic ecosystems.

Only a fraction of total mercury in water is in the form of methylmercury, suggesting that inorganic mercury may not be the limiting factor in methylation. For example, Krabbenhoft et al (1999) collected water, sediment and fish samples at 106 sites from 21 basins across the United States, to determine the relations between total mercury and methylmercury in water, sediments, and fish. Their results indicate that, on an average, methylmercury constituted less than 5% of the total mercury concentrations in the water column.

As described above, methylation of inorganic mercury may be limited by the bioavailable fraction of mercury, which in turn is affected by other environmental parameters. Due to the site-specific dominance of one or more of these parameters on methylation processes, total and methylmercury concentrations are seldom correlated in natural aquatic environments. For example, excluding the one data point from a mercury-contaminated mine site in Nevada from Krabbenhoft's data (Krabbenhoft et al 1999), no correlation was found between total and methylmercury concentrations in water samples collected across the United States. Similarly, total mercury concentrations account for almost none of the variance in methylmercury concentrations ( $R^2 = 0.007$ , N = 38) in various streams in the Experimental Lakes Area in Northwestern Ontario, and sites with one of the highest total mercury concentration had the lowest average methylmercury concentration (Kelly et al 1995). Other examples come from recent mercury TMDLs in Georgia, where the EPA collected total mercury and methylmercury samples of water, sediments, and fish. No significant relationship was found between these two parameters in the Savannah River water column data ( $R^2 = 0.003$ ) or in water column

data from South Georgia rivers ( $R^2 = 0.28$ ). The absence of this relationship has been observed between total mercury and methylmercury in a number of other studies (Cope et al 1990; Monson and Brezonik 1998; Gilmour et al 1998).

It is noted that mercury levels in fish from some of the most mercury-contaminated sites are comparable or lower than the mercury levels observed in the relatively pristine areas with some of the lowest total mercury concentrations. For example, in the South Yuba River, Deer Creek, and Bear River drainages of California, whose watersheds contain abandoned gold mining sites where mercury was used to extract gold from gold-bearing ores, May et al (2000) measured mercury levels in fish. Mercury concentrations in largemouth bass ranged from 0.20 to 1.5 ppm, comparable to the levels in the same species in South Georgia rivers (0.18 to 1.4 ppm), where there are few if any significant point sources, and the Savannah River (0.14 to 1.44 ppm), to which a chloralkali plant and the Savannah River Department of Energy (DOE) site discharge.

Kelly et al (1995) concluded that, "total mercury concentration is not a good predictor of methylmercury concentration in stream water or in lakes in general, but it appeared to be a good predictor for lakes within individual geographic areas" (such as some Wisconsin Lakes, where a strong correlation exist between total and methylmercury; Watras et al 1998), and even in those cases, "a predictive relationship determined in one region may not be useful in another." This conclusion is supported further by the data from the nationwide study conducted by Krabbenhoft et al (1999), where sub-basins with mining operations that had the highest total mercury concentrations in sediment and water had low methylation rates, whereas methylation rates were highest in basins with more wetlands. This is in agreement with the conclusion reached by Gilmour et al (1991) that, "in general, the percentage of methylmercury does not appear to be a function of total mercury, i.e. contaminated systems do not have consistently higher or lower % methylmercury than pristine waters."

As most of the methylation occurs in sediments,<sup>11</sup> we investigated the relationship between total and methylmercury in sediments in several studies and found no consistent relationship between these two parameters in sediments as well. Review of data collected by Krabbenhoft et al (1999) indicates that total mercury explains little of the variance in methylmercury in sediments ( $R^2 = 0.24$ , N = 105). When mercury and methylmercury concentrations were normalized to LOI (loss on ignition), the relationship is improved slightly ( $R^2 = 0.34$ ), but when the outliers (mercury-contaminated sediments from mine-site) were removed, there was no relationship between total and methylmercury ( $R^2 = 0.03$ , N = 102). This lack of relationship may be due to the overriding influence of various geochemical parameters described above on methylation<sup>12</sup>.

## 4.2.1.2.1 Knowledge Gaps

Recent approaches to specifying mercury load reductions in point and nonpoint sources have implicitly assumed that reductions in (total) mercury loading will proportionately

<sup>&</sup>lt;sup>11</sup> Note that water column methylation may be important because the volume of water is typically much larger than the volume of surficial sediments.

<sup>&</sup>lt;sup>12</sup> Krabbenhoft et al (1999) found a better relationship ( $R^2 = 0.68$ ) by basin-averaging values of LOI-normalized total and methylmercury.

reduce methylmercury concentrations in aquatic environments and, thus, decrease mercury levels in fish. Furthermore, translating a fish tissue-based criterion into a water column-based criterion for methylmercury also assumes that methylmercury concentrations in fish are proportional to total mercury concentration in the water column. These assumptions are reflected in EPA's statements in recent mercury TMDLs, where the Agency has concluded that "reductions in (total mercury) loadings will lead to proportional mercury loading reductions in all media," and that "there may be a large degree of scientific uncertainty regarding the rates at which methylation rates take place, but there is general scientific agreement that more mercury in the environment results in more mercury in fish" (US EPA 2001d). EPA Region 4's assumptions and conclusions appear to be in contrast to the evidence in the literature, some of which is reviewed above. These assumptions would hold true only when production and bioaccumulation of methylmercury is driven solely by the quantity of inorganic mercury in the aquatic environment, which clearly is not the case. As described earlier, methylmercury production in aquatic environments is controlled by a number of synergistic and antagonistic biogeochemical factors, including the amount of mercury that is bioavailable for methylation, but is not directly dependent on total mercury concentrations in the system.

## 4.2.1.2.2 Implications of Knowledge Gaps

Current attempts to establish water quality standards for total mercury based on methylmercury in fish are founded on assumptions that have not been verified to date or supported by field data. It may be possible that the ongoing METAALICUS project (Harris et al., 2001) may answer some of the questions on how fish respond to changes in atmospheric loading rates. Until those results are available and we are able to model the production of methylmercury in the environment and determine the relationship between total and methylmercury, developing strict numeric criteria for total mercury in order to meet certain levels in fish cannot be defended scientifically. While use of the methylmercury/Hg<sub>tot</sub> ratio (fraction methylmercury) might be a reasonable predictor of methylation "efficiency" in aquatic systems (Gilmour et al 1998), using that ratio to derive water quality standards (or for translating fish concentration to total mercury concentrations) is inappropriate because it incorrectly assumes that a proportional relationship exists between total and methylmercury in water.

## 4.2.2 Mercury and Methylmercury Sampling Issues

Measuring mercury and methylmercury in environmental samples requires clean sampling methods and specialized training and, consequently, is very expensive. If criteria are to be developed for mercury concentrations in the aquatic environment, spatial and temporal variations of mercury and methylmercury concentrations in various media (fish, sediment, water) and the analytical challenges associated with their measurement must be taken into consideration. Here we outline some of these issues based on our review of recent mercury TMDLs.

#### 4.2.2.1 Spatial Variation

Water quality targets (WQTs) for mercury have been proposed on a watershed-scale basis using average concentrations of mercury and methylmercury in water and fish samples collected from a limited number of locations in the watershed. (For example, recent mercury TMDLs done in South Georgia watersheds were based on sampling data from only 2 or 3 locations in each watershed). However, mercury concentrations in these media are not distributed uniformly within any one watershed due to a number of factors (e.g., higher loads of mercury from a tributary or a point source, localized regions of anoxia that favor methylation, heterogeneity of food web structure in various parts of the system, mobility of fish within the water body, etc).

Watras et al (1998) measured mercury species in 15 northern Wisconsin lakes over a period from 1990 to 1994 and reported the mean and standard deviations of the measured mercury species. Mean total mercury ranged from 0.52 ng/L to 4.36 ng/L and total methylmercury concentrations ranged from 0.04 ng/L to 0.83 ng/L. Coefficients of variation<sup>13</sup> (CVs) ranged from 77% to 2.3% for total mercury and correlated negatively with the mean (r = - 0.51). CVs for total methylmercury were higher as a rule, ranging from 75% to 84%, and were correlated negatively with the mean (r = -0.71). The mean CV for total mercury was 26% and the mean CV for total methylmercury was 43%.

Depending on the spatial distribution of sampling locations, such heterogeneities can introduce a large uncertainty in the estimated water quality criterion. In the case of the Savannah River TMDL, for example, EPA collected water and fish samples from 16 locations within the watershed, both from the tributaries and from the main stem of the river. The CV in this data set was 71% for total mercury in water, 107% for methylmercury in water, 132% for fraction methylmercury in water, and 84% for mercury concentrations in fish tissue. Data collected by scientists at the DOE's Savannah River Site (SRS) from more spatially limited portions of the Savannah River had somewhat lower CVs. In the SRS data, water samples collected about the same time showed that the filtered (i.e., dissolved) total mercury concentrations had a CV of 40% (N = 24), while the unfiltered total mercury had a CV of 78% (N = 25). Analysis of fish tissue samples collected over a three-year period (1993-1996) had a CV of 48% (N = 407).

From the above examples, it is apparent that there is a certain degree of spatial variability that cannot be avoided even with extensive sampling (e.g., 48% variability in fish tissue concentrations in SRS data even with 400+ samples). That is, spatial and temporal variability are the rule, rather than the exception. Because the effects of spatial variability will be different among water bodies, it is difficult to recommend numbers of samples that should be collected in a given watershed. However, it is important to collect an adequate number of samples to adequately characterize the water body. This means taking the typical variability demonstrated above into consideration and collecting an adequate number of samples in order to quantify the variability and account for it in the regulatory decision making process. Spatial heterogeneity of the watershed, physical and chemical variations within a water body, and any prior information on water quality and/or trophic structure all should be taken into consideration in determining sampling frequency and location.

<sup>&</sup>lt;sup>13</sup> The coefficient of variation (CV) is equal to the standard deviation divided by the mean and expressed as a percentage.

Due to the lack of steady state conditions within watersheds, total mercury is not persistent in the water column. For instance, it is converted to other species, precipitated, and adsorbed to sediments (becoming associated with bottom sediments) at different rates in different parts of the aquatic ecosystem. Because of variations in net methylation rates within a given watershed, total mercury concentrations in the water column are not proportional to changes in methylmercury concentrations in the water column (as reflected by poor correlations between total and methylmercury in water). For example, even though the total mercury concentrations in the tributaries and main stem of Savannah River were comparable (3.7 ng/L vs. 3.3 ng/L), methylmercury concentrations in water and in fish from tributaries were from 2 to 4 times higher than the levels in main stem of the river (US EPA 2000f).

## 4.2.2.2 Temporal Variation

Another important source of uncertainty arises from doing "snapshot" sampling in water bodies that show large seasonal or year-to-year variations in total and methylmercury concentrations. A number of studies have confirmed that mercury and methylmercury concentrations vary seasonally in the water bodies (Wang and Driscoll 1995; Monson and Brezonik 1998; Watras et al 1994). Changes in mercury loads often are related to runoff events in streams, the redox cycle in stratified lakes, concentrations of organic matter and oxyhydroxides (Ullrich 2001), and changes in temperature and pH. Generally, methylation rates are thought to be higher in summer due to higher temperatures, increased microbial activity, and higher organic carbon content associated with higher productivity.

Changes in mercury and methylmercury concentrations between different sampling events can cause large variations in calculated mercury loads and water quality targets. For instance, EPA collected water and fish samples from six watersheds (Alapaha, Ochlocknee, Satilla, St. Mary's, Suwannee, and Withlacoochee) in the summer of 2000 and in the spring of 2001. In figures 4-1 (a - e) below, concentrations of total mercury, fraction methylmercury, calculated BAF, and water quality targets based on these parameters are compared between these two data sets.











# Figure 4-1. Comparison of total mercury in water, methylmercury in water, fraction methylmercury in water, bioaccumulation factors and water quality targets in six South Georgia Rivers sampled in 2000 and 2001.

Total mercury concentrations measured in 2000 and 2001 are substantially different in some watersheds. For example, the total mercury concentration in the Alapaha River was 3.5 ng/L in 2000 and 15.1 ng/L in 2001 (a 430% increase). Similarly, the concentrations in the Ochlockonee River changed from 1.49 ng/L to 9.08 ng/L (a 609% increase). The concentration in the Withlacoochee River increased by 298%. Due to the lack of persistence of inorganic mercury in the water column, such temporal variability is not surprising. Differences between 2000 and 2001 data are observed for methylmercury as well. It is noted that 2000 sampling occurred during a drought with low water levels and lower flows, compared with 2001 sampling, which was conducted during a relatively wet period with high water levels and flows. Despite the increase in total and methylmercury concentrations in 2001 samples, the fraction methylmercury is comparable in 2001 and 2000 samples.

Calculated bioaccumulation factors also showed large apparent variations between the two datasets, largely due to changes in methylmercury concentrations in water (the average fish tissue concentrations remained relatively the same). For example, the average calculated BAF for trophic level 4 fish in the Ochlockonee River decreased from 4,170,000 L/kg in 2000 to 610,000 L/kg in 2001. On the other hand, the average calculated BAF in the Suwannee River increased from 2,610,000 L/kg in 2000 to 4,760,000 L/kg in 2001. Variations in BAF were not consistently related to variations in total mercury concentrations during these two years.

Even though EPA averaged the two datasets to calculate the new water quality target for each watershed, variations of the order of 600% in BAF and other factors point out some real uncertainties associated with one time sampling of water bodies. For example, in the Alapaha River, had the TMDL been established using only the 2000 data, it would have resulted in a water quality target of 1.09 ng/L compared with a target of 6.79 ng/L using the 2001 data (a 523% increase in WQT) (Figure 4-1e), despite the fact that total mercury concentration in 2001 was more than 4 times higher than in 2000 sampling. We strongly recommend that adequate data be collected to effectively mitigate such year-to-year (and seasonal) variations before establishing numerical water quality standards.

#### 4.2.2.3 Analytical Issues

While mercury has been recognized as an environmental pollutant for several decades, sample contamination and lack of sensitive instruments have hampered low-level mercury analysis until the early 1980's. With the evolution of sensitive analytical methods, different species of mercury have been quantified accurately in environmental samples. Recently, EPA has developed Method 1631 to provide reliable measurements of mercury at EPA water quality criterion levels (US EPA 2001e). This method has a Method Detection Limit (MDL) of 0.02 ng/L when no interferences are present and a minimum level of quantitation of 0.5 ng/L.

Unlike the analysis of total mercury, EPA Method 1630 for methylmercury analysis is still in the draft form and has not been finalized. It also has not been subjected to an interlaboratory validation study to assess its expected performance when used by multiple laboratories. This is a fundamental shortcoming in the mercury regulatory process.

Method 1630 has a method detection limit (MDL) of 0.02 ng/L when no interferences are present. In recent TMDLs, values as low as 0.02 ng/L have been reported and used in calculating fraction methylmercury and BAF (US EPA 2000f). These reported values are substantially lower than the QC acceptance criteria for method blanks (maximum 0.10 ng/L; mean 0.05 ng/L), laboratory blanks (0.07 ng/L in Battelle's sample analysis for Savannah River TMDL) and field blanks measured in TMDL sampling (e.g., in South GA TMDL, the average field blank for methylmercury was 0.03 ng/L, with a maximum of 0.11 ng/L). Additional uncertainty and upward biasing of the BAF is attributable to the direct use of test results that, even if above the detection level, are below the level at which they can be reliably quantified (i.e., below the quantitation level). The obvious problem is that extremely high BAF values are calculated due to very low concentrations of methylmercury in water and not because the fish are grossly contaminated. This is illustrated by the Savannah River data (Figure 4-2), where most of the high BAF values are a result of very low methylmercury concentrations in water (7 out 8 BAF values  $\geq 5$  million had methylmercury concentrations below 0.1 ng/L).



Figure 4-2. Comparison of BAF to methylmercury concentrations in water for the Savannah River (Data source, US EPA 2000f)

Olson and Dewitt (1999) point out that there are no certified standards or certified reference materials for methylmercury analysis. In addition, there has been considerable controversy in recent years regarding the "true" methylmercury content of environmental samples (particularly sediments and organic rich waters) after it was shown that methylmercury could be generated artificially during the sample preparation process (Hintelmann et al 1997). Considering these factors together with the field and laboratory blank issues described above, we strongly recommend that values below 0.1 ng/L not be used in calculating BAF or WQT.

Other problems include reproducibility of results between two analytical laboratories. For instance, in the Savannah River samples, EPA and DOE's SRS split samples of fish and water for mercury analysis. EPA's samples were analyzed by Battelle and SRS' samples were analyzed by Frontier Geosciences, Inc. While EPA and SRS results for mercury in fish tissue were comparable, EPA's methylmercury analytical results for water samples were, on average, 30% lower than the results of SRS' analysis (US EPA 2000f). Because the fish results are about the same, the use of one or the other data to calculate BAFs would result in a 30% difference for the BAF and the water quality target.

## 4.2.2.4 Knowledge Gaps

Mercury and methylmercury concentrations within a water body can exhibit considerable spatial and temporal variability, affecting calculated loads, BAFs, water quality targets, and load allocations. One-time sampling of the water column is inadequate to establish relationships because methylmercury production can vary substantially depending on the sampling season. Spatial variability in mercury and methylmercury concentrations also is important to consider because it can introduce large uncertainties in the calculated water quality criterion. Because each aquatic system exhibits different degrees of spatial and temporal heterogeneity, it is difficult to determine in advance how many samples need to be collected from each water body. Sampling intensity and frequency should consider known physical/chemical variability within the water body, variability within the collected data and the uncertainty and margin of safety required in TMDL calculations. Finally, including very low methylmercury concentrations (values near the MDLs and field/laboratory blank values) can result in unrealistically large BAFs. It is recommended that field and blank values for methylmercury be monitored carefully, and field-observed values below 0.1 ng/L not be included in BAF calculations.

## 4.2.2.5 Implications of Knowledge Gaps

Spatial and temporal variability in mercury and methylmercury concentrations can introduce very large uncertainties in the estimated loads and the calculated water quality criterion. It may be difficult to quantify such uncertainties without adequate sampling. While fish tissue mercury concentrations tend to integrate seasonal and daily variations in methylmercury production, snapshot sampling of methylmercury in water can result in misleading BAF values and the percentage of methylmercury. This can in turn result in unrealistic water quality standards, load allocations, and unreasonable differences in standards between portions of the same water body or among regionally similar water bodies.

#### 4.2.3 Mercury Bioaccumulation

The bioaccumulation of mercury in fish and subsequent ingestion represents a key exposure pathway for humans and wildlife. Exposure is predicated upon the quantity of fish consumed by the receptor and concentration of mercury in the fish tissue. Bioaccumulation of mercury takes place to an extent at all levels in the aquatic food chain, primarily as methylmercury. As there appear to be step-like changes in concentrations between trophic levels, attempts have been made to quantify bioaccumulation to organisms by their position in the food web. However, there are substantial differences among species within the same trophic level, presumably resulting from differences in life history, diet, and possibly metabolic differences and depuration rates. In order to accurately estimate exposures, both fish consumption rates and tissue concentrations in the consumed species must be accurately known. Unfortunately, both of these factors are subject to considerable uncertainty. Fish consumption as a factor in exposure assessment has been discussed previously, so the following discussion focuses on the process by which mercury is bioaccumulated in fish tissues.

The process of bioaccumulation of appreciable levels of mercury in fish can be said to begin with the conversion of inorganic mercury to methylmercury, as described in the previous section. Although there has been some recent work on methylation processes at the cellular level, there still is appreciable debate as to the exact processes that are occurring. Morel, et al (1998) state that, at low concentrations, the cellular uptake of mercurv appears to be affected primarily by the diffusion through the lipid membrane of lipid soluble mercury complexes, particularly HqCl<sub>2</sub>. The net result being that chloride concentration and pH are the controlling factors for cellular uptake of mercury in oxic waters. In anoxic waters, it has been suggested that the uncharged di-bisulfide-mercury complex, Hg(HS)<sub>2</sub>, and the uncharged polysulfide complexes, HgS<sub>n</sub>, play an important role in mercury bioavailability. Like that of inorganic mercury, the authors suggest that the microbial uptake of methylmercury is facilitated by diffusion of its uncharged chloride complex, which has a lipid solubility similar to HgCb. Preferential bioaccumulation of methylmercury is thought to be a result of association of methylmercury and its assimilation with the soluble fraction of cells, while the inorganic mercury associates with the particulate cellular material and is thus excreted (Boudou and Ribeyre 1997).

As previously described, sulfate-reducing bacteria (SRB) are considered to be the principal methylators of inorganic mercury in estuarine and freshwater sediments. Benoit et al (1999) have proposed that the chemical speciation of mercury controls uptake into bacterial cells; specifically, that in sulfidic pore waters, HgS<sup>0</sup> readily crosses the bacterial membrane because it is small and uncharged. Implicit in their analysis is that mercury must enter cells to be methylated. In this work, mercury speciation was manipulated by growing *Desulfobulbus propionicus* across a range of sulfide concentrations with inorganic mercury added in the form of ground ores. Methylmercury production was found to be linearly related to the calculated concentration of HgS<sup>0</sup> in solution, and passive diffusion of HgS through the cell membrane was found to be sufficient to support methylmercury production by cells.

Once methylation has occurred, whether in the water column or in sediments, methylmercury is found in aquatic ecosystems in sediments, pore water, and in water overlying sediments. Because methylation appears to be microbially mediated to a great extent, the process itself results in the transfer of mercury into biota at the lowest and most fundamental level of the ecosystem and food chain.

Methylmercury has been documented in biota at all trophic levels of aquatic ecosystems. At lower trophic levels, methylmercury appears to make up a smaller proportion of total mercury in biota. At higher trophic levels, it appears to constitute higher proportions of the tissue burden (Watras et al 1998). For instance, percent methylmercury in lower trophic levels of pelagic food webs in 15 Wisconsin lakes averaged 11% in DOC, 18% in microseston, 57% in zooplankton, and 95% in small fish (Watras et al 1998). A similar effect was noted in Onondaga Lake, New York, where methylmercury values were about 5% of total mercury in the water column, 22% in phytoplankton, 40% in zooplankton, and 97% in fish (Becker and Bigham 1995). Morel et al (1998) explain the observation of relatively high methylmercury content in fish by suggesting a high specificity of the intestinal wall in fish for methylmercury. Inorganic mercury, which apparently is adsorbed at the microvilli interface, is absorbed at a much lower rate.

## 4.2.3.1 Role of DOC in Bioaccumulation

Dissolved organic carbon plays an important role, not only by affecting mercury bioavailability for methylation, but also by complexing with methylmercury, which alters its availability to the food chain. DOC clearly appears to enhance the solubility of mercury by preventing the precipitation of mercury by sulfides. Aiken et al (1998) found that mercury was precipitated as meta-cinnabar under mildly reducing conditions and pH < 7. However, DOC prevented the precipitation of mercuric sulfide at a concentration of 20 mg C/L. Ravichandran et al (1998, 1999) observed that precipitation and aggregation of meta-cinnabar was inhibited in the presence of low concentrations (~3 mg-C/L) of humic fractions of dissolved organic matter (DOM) isolated from the Florida Everglades.

DOC also appears to enhance the solubility of mercury by complexation to nonsettleable fine particulates and colloids. Miskimmin (1991) demonstrated that the presence of DOC increased concentrations of methylmercury in water as evidenced by decreasing partition coefficients with increasing DOC. Watras et al (1998) observed that concentrations of dissolved total mercury and methylmercury depended strongly on DOC concentrations in 15 Wisconsin lakes. Babiarz et al (2001) studied the partitioning of total and methylmercury to freshwater colloids and found that the amount of total mercury sequestered on colloids was lower in waters with higher conductivity. Colloidal phase concentrations of total mercury correlated poorly with filtered organic carbon; however, methylmercury correlation with organic carbon was stronger. Cai et al (1998) found that inorganic mercury in the Everglades was associated mainly with colloids rather than the particulate or dissolved fractions. On the other hand, methylmercury appeared to be associated mainly with the dissolved fraction and very small (< 3 kDa) colloids. In fact, methylmercury was linearly correlated with DOC size fractions.

While the effect of DOC is clearly to maintain more mercury in a dissolved state, the larger question is, does this inhibit or enhance bioaccumulation? Driscoll et al (1996) studied mercury biogeochemistry in thirty-two acidic Adirondack lakes. Methylmercury in yellow perch was correlated with DOC concentrations in these lakes, which was in turn observed to be a function of the quantity of wetlands in the drainage. Aluminum concentrations showed the strongest correlation with mercury in fish. The authors postulated that through the release of DOC, wetlands were providing methylmercury to
the lake ecosystem, but that competition with aluminum ion may decrease the binding of methylmercury to DOC making it more available for biological uptake. Watras et al (1998) found that increasing DOC levels *decreased* the partitioning of methylmercury to microseston in 15 Wisconsin lakes. Gilmour and Henry (1991) report that increased levels of DOC in the water column result in *lower* methylation rates despite the increase in microbial activity, presumably due to the sequestration of dissolved mercury by organic ligands. Barkay et al (1997) reported that increasing DOC reduced the bioavailability of Hg(II) and that this reduction was more pronounced under neutral rather than acidic conditions. Grieb et al (1990) reported a negative correlation of fish tissue concentrations and DOC. Harris et al (1996) applied the R-MCM (Regional - MCM) model to data from 23 Wisconsin lakes. After calibrating the model with data from 7 lakes, water column concentrations of total mercury and methylmercury in the remaining 16 were predicted reasonably well except in two lakes with high DOC levels. Predicted methylmercury in fish was maximized at DOC concentrations of about 8-10 mg/L. Boudou and Ribeyre (1997) reported that, with increasing DOC up to about 8 mg/L, mercury concentrations in fish increase, but samples taken from dystrophic lakes (having DOC > 20 mg/L) showed lower bioaccumulation.

Thus, while DOC appears to associate with mercury, making it perhaps *less* bioavailable for uptake by organisms, there are a number of studies that show increasing bioaccumulation with increasing DOC. On a national scale, high levels of methylmercury in fish appear to be associated with water bodies having high concentrations of DOC (Brumbaugh et al 2000). Richardson et al (1995) found a positive correlation between fish tissue levels and DOC concentrations. Further support for this comes from data collected by the Georgia Environmental Protection Division (GA EPD) and EPA Region 4, which show that the highest mercury concentrations in fish tissue occur in waters of the Coastal Plain where DOC levels are highest. This may be because abiotic mercury methylation is enhanced by humic substances (Weber 1993). DOC also helps to retain mercury in the water column where methylation may occur.

# 4.2.3.2 Bioaccumulation in Lower Trophic Levels

Bioaccumulation of methylmercury in the lower trophic levels is important as it represents the foundation for biomagnification into higher trophic levels and ultimately into consumable fish. Watras et al (1998) showed that log partition coefficients for methylmercury in microseston of 15 Wisconsin lakes were on the order of 4.8 to 6.2, indicating that uptake by microplankton is a major step in the bioaccumulation process. Bioaccumulation factors for higher trophic levels increased only by a factor of two to four. Additionally, their data support a hypothesis of active, rather than passive, uptake by these organisms, and suggest that the supply of methylmercury is not a limiting factor for uptake by these organisms. Concentrations in zooplankton were correlated with, and higher than, concentrations in microseston with proportionally higher percentages of methylmercury, consistent with observations by a number of other researchers. Methylmercury concentrations in crustacean zooplankton were enhanced at lower pH.

Cleckner et al (1998) studied trophic transfer of methylmercury in the northern Florida Everglades with emphasis on the lower trophic levels. They found that methylmercury accumulation in periphyton did not appear to be a simple partitioning from the water, suggesting an active uptake mechanism similar to the observation by Watras et al (1994, 1995, 1998) from Wisconsin lakes. They also found that methylmercury levels in periphyton varied seasonally and spatially within the study area. Seasonally, levels in periphyton peaked at different times of the year in different parts of the study area. Methylmercury as a percent of total mercury in periphyton ranged from 1.2% to 27.5%. Spatially, concentrations in periphyton were lowest in the northern eutrophic portions of the study area, and highest in the southern oligotrophic areas. The percent methylmercury also increased from north to south in at least one season. Seasonal effects in higher trophic level organisms (i.e., *Gambusia*) were postulated to be associated with seasonal changes in diet. Effects of this type may be masked by an unknown lag time between seasonally high methylmercury in the water column and corresponding peak concentrations in organisms. In contrast to the microplankton data of Watras et al discussed above, tissue levels in fish were on the order of 8 to 130 times higher than in periphyton in the Everglades.

Serdar et al (2001) found levels of mercury in signal crayfish ranging from 0.05  $\mu$ g/g to 0.54  $\mu$ g/g in Lake Whatcom, Washington, collected in May and June of 2001. Spatial differences were noted with the highest mean and median levels occurring in the largest and deepest part of the lake (Basin 3). Levels were lowest in the shallow Basin 1, which nearly is surrounded by development from the City of Bellingham. The median concentration in Basin 3 (0.102  $\mu$ g/g) was almost twice that of the median level in Basin 1 (0.058  $\mu$ g/g). These levels approach those found in fish from Lake Whatcom.

Slotton et al (2001) studied bioaccumulation in lower trophic levels in Cache Creek, California, portions of which historically have been affected by mining. They sampled benthic invertebrates over four seasons (February, May, August, and November) in 2000 and reported that most predatory taxa exhibited relatively consistent methylmercury levels. Levels in herbivorous species were significantly lower. Interestingly, the percent methylmercury was relatively high in these invertebrates (77% to 93%), except in nearmine locations where the percentages were much lower (17% to 39%). They also found that a significant portion of the overall variation in invertebrate methylmercury was attributable to aqueous mercury concentrations. The best indicator of invertebrate methylmercury was filtered total mercury and aqueous particulate total mercury, indicating that winter storm pulse loadings may be relevant to bioaccumulation in these systems. However, they point out that aqueous concentrations alone cannot predict concentrations in fish tissue. Log BAFs for aquatic invertebrates were calculated using mean raw water methylmercury concentration for the hydrologic period prior to sample collection. Values ranged from about 5 to 6.

These studies indicate that there is considerable variation in, and important unanswered questions about, the uptake of mercury by primary producers and lower trophic levels in the aquatic wood web.

#### 4.2.3.3 Bioaccumulation in Fish

The bioaccumulation of mercury in consumable fish is of ultimate interest because this is the vector by which humans and upper trophic level wildlife are exposed. Bioaccumulation of methylmercury occurs in fish due to its ionic nature that facilitates penetration of membranes and its strong affinity for sulfyhydryl groups in proteins of the muscle tissue (Wiener and Spry 1994). The binding of methylmercury by these organosulfur groups in the muscle proteins prevents significant loss of methylmercury due to elimination or depuration. Because the uptake of mercury appears to be a relatively slow process, tissue concentrations appear to increase over time, with larger fish typically exhibiting higher concentrations than smaller fish of the same species.

Watras et al (1998) found that methylmercury concentrations in yellow perch were influenced strongly by the pH of the lake and to a lesser degree by DOC, with low pH and high DOC tending to enhance methylmercury concentrations in fish. They found that microseston, zooplankton, and fish were enriched in methylmercury relative to DOC by factors of 3, 5, and 20, corresponding to biomagnification factors ranging from 1.6 to 4 between trophic levels. Effects of DOC on BAFs for microseston, zooplankton and fish were similar.

Fish in Lake Whatcom, Washington, exhibited spatial differences in total mercury concentration and among species types. In smallmouth bass, a trend was observed in which larger fish had higher total mercury concentrations. Concentrations in this species were highest among the six finfish species collected ( $0.49 \ \mu g/g$ ) and were higher in larger bass regardless of where they were collected in the lake. Smallmouth bass levels were significantly higher in 2000 than in a previous 1998 survey. Yellow perch had the next highest levels ( $0.20 \ \mu g/g$ ). Cutthroat trout, another top-level predator, had the least tendency to accumulate mercury, with tissue concentrations averaging only 0.07  $\mu g/g$ . Tissue concentrations were highest in Basin 3, the largest and deepest part of the lake, even though the highest concentrations in sediment are in Basin 1, which is in closest proximity to the City of Bellingham. Depletion of hypolimnetic oxygen observed in Basin 1 also would suggest a stronger likelihood of production of methylmercury, but fish tissue concentrations do not confirm such an hypothesis. Size and age of fish did not appear to account for differences between the three lake sub-basins.

Salinity of the water body appears to have a pronounced effect on bioaccumulation. Gilmour and Riedel (2000) surveyed fish taken from the freshwater and estuarine sections of the Chesapeake Bay. Striped bass and largemouth bass taken from the estuary were observed to contain less mercury than counterparts of the same size and species from freshwaters. Barkay et al (1997) have suggested that increased chloride concentrations result in a relative abundance of negatively charged HgCl<sub>3</sub><sup>-</sup> and Hg Cl<sub>4</sub><sup>2-</sup> species and, consequently, that the bioavailability of Hg(II) for microbial transformations should be reduced in estuarine and marine environments versus freshwater environments.

Slotton et al (2001) found that large fish mercury concentrations generally were highest at sites with the most elevated levels of aqueous and invertebrate total and methylmercury concentrations and vice versa. Anomalies were apparent in the data; for instance, in Upper Bear Creek, CA, a low gradient, clear water, high nutrient, high biological activity site, fish had unusually elevated mercury levels, but median aqueous total mercury levels were the lowest among all sites sampled in the Cache Creek watershed.

4.2.3.4 Variability in Biota and Fish Tissue Concentrations

A number of researchers have commented on the variability among biological species and even among similarly aged members of the same species and in water bodies having similar morphophetric characteristics and atmospheric inputs (Scheuhammer and Graham 1999; Boudou and Ribeyre, 1997). This variability manifests itself both temporally (seasonally and from year to year) and spatially (across and within lakes and river systems). Variations in fish are no doubt to some extent driven by variations of methylmercury in the water column, and a number of researchers have pointed out these variations. For instance, Watras et al (1994) reported seasonal variations in total mercury and methylmercury in Little Rock Lake, Wisconsin. Total mercury concentrations tended to be high in the summer and low during winter. Winter declines were attributed to lower atmospheric inputs during this season due to the formation of an ice cover. During summer, methylmercury tended to increase, perhaps in response to warmer temperatures and enhanced productivity.

Monson and Brezonik (1998) reported seasonal patterns of mercury species in soft water Minnesota lakes. Methylmercury declined throughout the growing season. Total mercury also sharply declined from spring to summer but increased again in the fall. Concentrations in plankton were lowest in spring and rose to higher levels in summer. The mass of mercury increased in plankton from spring to fall, as did the methylmercury fraction. BAFs for mercury increased over the growing season. Overall, the log BAF for total mercury in net plankton (wet weight) was 4.45. Log BAFs for methylmercury in plankton ranged from 4.9 to 5.43.

Porcella (1994) reported that mercury concentrations in yearling perch in seven lakes within the same region of northern Wisconsin varied over an order of magnitude. Differences were greater than could be explained by differences in pH and DOC alone, although pH was clearly important. Other chemical factors such as chlorophyll-a, sulfate, chloride, and calcium varied by factors of 2 among the lakes and appear to be responsible, in part, for some of the differences. Mercury in these fish was correlated with methylmercury in the water column.

In the South Yuba River, Deer Creek, and Bear River drainages of California whose watersheds contain abandoned gold mining sites where mercury was used to extract gold from gold-bearing ores, May et al (2000) measured total mercury levels in fish. Black bass, including largemouth, smallmouth, and spotted bass, ranged in concentration from 0.20 to 1.5 ppm, sunfish ranged from less than 0.10 to 0.41 ppm, channel catfish ranged from 0.16 to 0.75 ppm, rainbow trout from 0.06 to 0.38 ppm, and brown trout from 0.02 to 0.43 ppm.

Suns and Hitchin (1990) report on the variability in fish tissue concentrations in 16 Canadian lakes over a 10-year period from 1978 to 1987. Mean total mercury tissue values ranged from 32 to 233 ng/g. Among lakes, bioaccumulation in fish varied with pH, with higher fish tissue concentrations associated with lower pH. CVs ranged from 16% to 54%, with higher values of CV tending to be associated with lower means (r = -0.71). CV of fish length ranged from 3.1% to 18%; therefore, variability in tissue concentrations was greater than could be accounted for by size differences alone.

Gill and Bruland (1990) report the variability of (presumably total) mercury concentrations in fish tissue from California lakes. Mean tissue concentrations ranged from 0.10 ppm to 2.5 ppm and CVs ranged from 7.5% to 60%. The highest CV was associated with the lowest mean and, in general, lower CVs were associated with higher means (r = -0.26).

Differences in fish tissue concentrations can by no means be explained solely by differences in water chemistry or methylmercury concentrations. Fish exposed to the same levels of methylmercury in water may exhibit different levels of body burden due to differences in the concentrations in consumed prey. Thus, food web dynamics may also play a significant role in bioaccumulation from water and sediments to lower trophic level organisms and, thence, to higher trophic level organisms.

#### 4.2.3.5 Variability Among Fish Species within the SameTrophic Level

Table 4.1 shows typical mercury in tissue from trophic level 3 and trophic level 4 fish collected in various locations in the United States. This data is interesting in several ways. First, it demonstrates that, overall, trophic level is an important factor in determining the mercury content of fish tissue. Values for trophic level 3 fish range from 0.01 mg/kg to 1.43 mg/kg, while trophic level 4 fish range from 0.04 mg/kg to 3.98 mg/kg.

Thus, there appears to be an increase of about a factor 4 from trophic level 3 to trophic level 4 fish when all the data are considered.

Second, the fish tissue values are consistent for any given species when compared from location to location. For instance, yellow perch concentrations range from 0.02 mg/kg to 0.87 mg/kg. Sunfish range from 0.29 mg/kg to 1.00 mg/kg. There also is consistency between data on brown bullhead and channel catfish from diverse locations. The same holds true for smallmouth bass, largemouth bass, other bass species (primarily black bass and spotted bass), and chain pickerel in these studies. These data seem to indicate that certain species tend to bioaccumulate mercury within certain ranges, regardless of the status of the water body with regard to mercury loading and environmental factors.

Third, there is considerable variability in fish tissue concentration within each trophic level. For instance, channel catfish seem to have the ability to bioaccumulate mercury to a greater extent overall than yellow perch, sunfish, or even brown bullhead, a similar species. Similarly, even though walleye and chain pickerel are defined as top level aquatic predators, like largemouth bass, concentrations overall tend to be lower in these species. In brown trout, they are lower yet. This data seem to indicate that although trophic level is an important determinant of fish tissue concentrations in general, it is a poor indicator of concentration for any particular species. The implication of this observation is that the calculation of bioaccumulation factors by trophic level may have severe limitations when it comes to predicting mercury concentrations for individual species in other locations.

These data also are compared in the table to the ranges found in EPA's national survey of mercury concentrations in fish. EPA's database is quite large in comparison and, thus, the maximum and minimum values in the data are expected to be larger. Data also are compared to the approximate 25<sup>th</sup> and 90<sup>th</sup> percentile values for some species.

#### 4.2.3.6 Effects of Fish Size

A number of researchers have observed relationships between fish size and mercury body burden. However, this is not always the case and it appears to depend on the fish species. Serdar et al (2001) observed a relationship between smallmouth bass length, age, and mercury concentration in all three basins of Lake Whatcom, Washington. Such relationships were observed in yellow perch in two of the three basins. However, for other species, there was no observed relationship between age, length, and mercury concentration. May et al (2000) found a significant relationship between mercury in smallmouth bass in Lake Englebright, California (CA). However, no relationship between fish length or mass and mercury concentration was observed for channel catfish in Rollins Reservoir, CA, for largemouth bass in Lake Combie, CA, or for spotted bass in Camp Far West Reservoir, CA. The data of Slotton et al (2001) show strong positive correlations (R<sup>2</sup> values from 0.69 to 0.95) between fish size and mercury in tissue across all sites sampled in Cache Creek, CA. Fish types included Sacramento pikeminnow, smallmouth bass and largemouth bass, and covered a wide range of fish weights from less than 100 grams to over 2000 grams.



Figure 4-3. Length versus mercury concentration for bowfin in the Savannah River (1994 – 1999)<sup>14</sup>

<sup>&</sup>lt;sup>14</sup> Data Source: South Carolina Department of Health and Environmental Control



# Figure 4-4. Length versus mercury concentration for largemouth bass in the Savannah River (1994 – 1999)<sup>15</sup>

In the Savannah River, data on individual bowfin collected by the State of South Carolina from 1994 through 1999 exhibit little relationship between length and mercury concentration ( $R^2 = 0.09$ ) as shown in Figure 4-3, above. However, as depicted in Figure 4-4, mercury concentrations in largemouth bass (non-detects removed from the data) were somewhat better correlated with length ( $R^2 = 0.40$ ) than in bowfin ( $R^2 = 0.09$ ). We note, however, that the removal of the data point (600, 2.58) from the largemouth bass data drops the  $R^2$  value to 0.20 from 0.40.

# 4.2.4 Overview of the BAF Approach

# 4.2.4.1 Bioaccumulation Factors

The bioaccumulation factor (BAF) has been used extensively to calculate biotic tissue concentrations from methylmercury concentrations in water (BAF = fish tissue concentration / water column concentration) and, more recently, to calculate water quality targets from allowable tissue concentrations. Because the mercury body burden in fish is primarily in the form of methylmercury, the denominator of the BAF is normally the methylmercury concentration in water. While the concept of BAF appears to be simple, caution should be exercised in using BAFs from one study to another because a variety of factors can affect the magnitude of this quantity. First, fish tissue concentrations could be either from whole fish, skin-on fillets, or from skinless edible muscle. Because most of the bioaccumulated mercury resides in the muscle, whole body levels or skin-on filets may be biased to lower concentrations and, thus, lower BAFs. Methylmercury concentrations in water are measured from either filtered or

<sup>&</sup>lt;sup>15</sup> Data Source: South Carolina Department of Health and Environmental Control

unfiltered samples. The construct used in the literature is usually that fish tissue concentrations are a function of dissolved methylmercury in the water column; therefore, filtered methylmercury samples would be the most appropriate. However, because methylmercury concentrations in fish diet are probably as, or more, important than dissolved methylmercury concentrations in water, some BAFs may be calculated based on total methylmercury in the water column. BAFs have been calculated using total or total dissolved mercury in the water column as well.

In its Mercury Study Report to Congress (US EPA 1997a), EPA summarized the literature available at that time regarding quantitative measurement and calculation of BAFs for fish. While bioconcentration factors (BCFs) were also reviewed by EPA along with predator/prey factors (PPFs) to convert from lower to higher trophic levels, for the purposes of this discussion, only that information applicable to estimating BAFs for trophic level 2, 3, or 4 fish directly from field data are reviewed. The information reviewed herein is taken from Appendix D.

A BAF of 1.6 x 10<sup>6</sup> L/kg was estimated to be applicable to trophic level 3 fish. Although EPA refers to these fish as planktivorous, it is more common that trophic level 3 fish are defined as omnivorous and include, for example, smaller centrarchids (e.g., sunfish, crappie, and bream), and bottom feeders (e.g., catfish). Trophic level 2 fish generally are considered planktivorous and would include shad, mullet and possibly bottom-feeders, such as carp.

This report contains BAF values for different types of fish, and these estimates came primarily from four sources. EPA estimated a BAF for gizzard shad of 667,000 using data in Becker and Bigham (1995). An average concentration in 3-4 year old shad was used along with a dissolved methylmercury concentration in water collected on a single day. EPA rightfully suggests that the uncertainty associated with this BAF is high because of the single day measurement of concentration in the water column. The methylmercury concentration was reported to be 0.3 ng/L.

The second BAF estimate was for yellow perch in Finland using the data of Rask and Verta (1995). The average concentration in perch collected over a three year period was used along with mean epilimnion dissolved methylmercury concentrations measured in a single day. Although EPA does not point it out in this case, the water column measurements from a single day also make this estimate highly uncertain. The methylmercury concentration was reported to be 0.103 ng/L.

BAFs were calculated for silversides and juvenile bass in Clear Lake, CA from the data of Suchanek et al (1993). Paired measurements of fish tissue concentrations and dissolved methylmercury in the water column were utilized. BAFs for the two species were similar, and an average value of  $1.53 \times 10^6$  was ultimately used in the analysis. The magnitude of the methylmercury concentrations was not reported by EPA.

A BAF for bloater in Lake Michigan was estimated from data provided by Mason and Sullivan (1997). A two-season (August/October) average dissolved methylmercury concentration was used to calculate the BAF. The methylmercury concentration in this study was very low (0.01 ng/L), probably lower than the detection limit for the analysis, which casts a shadow of uncertainty on the BAF value.

EPA used the four estimates derived above and calculated a geometric mean as a representation of central tendency for this trophic level. EPA also commented that information on fish species/size/age were limited or undeterminable for most of these studies. Other problems with the analysis include the fact that the gizzard shad in the study of Becker and Bigham are trophic level 2 fish; whereas the 3-4 year old yellow perch from the Finnish study are more likely to have feeding habits (small fish, insects, crayfishes and other invertebrates) more indicative of a trophic level 3 fish, as would the juvenile bass in the Clear Lake, CA study. This could explain why the BAF calculated for Lake Onondaga gizzard shad is roughly an order of magnitude less than the other estimates in this group. The silversides are likely trophic level 2 fish as they feed on copepods, mysids, and other planktonic crustaceans. In addition, two of the water bodies in these studies have been affected by direct industrial discharges, a chloralkali plant in the case of Onondaga Lake and gold mine runoff in the case of Clear Lake.

EPA also estimated BAFs for trophic level 4 fish in the same document using three of the same studies and one additional study. A BAF was calculated for 6-9-year old smallmouth bass and walleye (age class not given) using the data of Becker and Bigham from Onondaga Lake. Again, the dissolved methylmercury concentration was determined from a one-time measurement casting considerable uncertainty on the calculated BAF value of  $4 \times 10^6$ .

Trophic level 4 BAFs were calculated from data reported in Jackson (1991). The BAF value of 5.86 x 10<sup>6</sup> was an average from four lakes and represents a composite of two species; walleye (37-46 cm) and northern pike (55-71 cm). In this study, fish collection and water column dissolved methylmercury concentrations were taken in different years. EPA also indicates that this value should be viewed as a "minimum" given that the water column concentrations were analyzed using pre-1990's analytical methods. However, this "minimum" value turns out to be among the highest calculated from the four studies. Methylmercury concentrations are not provided in EPA's report.

A BAF for largemouth bass was calculated from data of Suchanek et al (1993). Fish tissue concentrations were estimated from graphs in the report showing the relationship between tissue concentrations and fish weight for each of the three lake areas. Data were used selectively for fish of greater than 450 grams (and up to 4200 grams). Fish tissue concentrations for each area were divided by dissolved methylmercury concentrations for each area, which had been measured over a two-year period. The calculated BAF was  $8.06 \times 10^6$ . EPA did not report methylmercury concentrations.

A BAF for lake trout in Lake Michigan was estimated from the data of Mason and Sullivan (1997). The value of  $1.14 \times 10^7$  also is subject to the same caveats as in the previous discussions of this report.

EPA calculated a geometric mean of  $6.81 \times 10^6$  based on the four estimates made from review of literature data. Using essentially the same studies, EPA made estimates of the BAFs for these species in these locales using dissolved total mercury rather than dissolved methylmercury. The derived estimates were  $1.25 \times 10^5$  L/kg for trophic level 3 fish and  $5 \times 10^5$  L/kg for trophic level 4 fish. A check on the validity of these values is to calculate the effective percent methylmercury for each trophic level by dividing the BAF for total mercury by the BAF for methylmercury. In the case of trophic level 4 fish, the effective methylmercury concentration is less than one percent (0.73%). In the case of the trophic level 3 BAFs, the effective methylmercury percentage is 0.78%. These

values seem very low and cast further doubt on the appropriateness of the calculated BAFs for the reported trophic levels. Finally, these BAFs were calculated from data originating primarily in northern lakes and may not be representative or appropriate for warm water systems, for riverine systems, or for systems with very different water chemistry, such as systems heavily influenced by wetlands.

Boudou and Ribeyre (1997) report that BCFs for methylmercury in Little Rock Lake were on the order of 3 million in yearling yellow perch and increased about 0.5 log units per trophic level. BCFs in Onondaga Lake also increased with higher trophic levels, ranging from  $8.3 \times 10^4$  for benthic macroinvertebrates to  $3.7 \times 10^6$  for piscivorous fish.

Using data from EPA Region 4 collected in support of TMDLs on the Savannah River and six South Georgia rivers, it is possible to calculate BAFs for individual fish as well as composites and individual species. Although this is *possible*, some of the same caveats should be made as have been made with EPA's estimation of BAFs in the Mercury Study Report to Congress. The principal drawback with the Savannah River data is that the methylmercury concentrations were measured one time, albeit at several locations in the river. In the case of the South Georgia TMDLs, water and fish data were measured in two different years, in two different seasons, with quite different results, pointing out the dangers of doing a one time snapshot sampling. The other major issue with calculating BAFs using EPA's 2000 and 2001 data from Georgia is that methylmercury concentrations are extremely low (resulting in extremely high BAFs), often near the method detection limit, while the field and laboratory blank values were considerably higher than the MDLs. In fact, BAFs calculated by EPA in these systems are much higher than previously reported elsewhere, even though they were calculated using total methylmercury in the water column rather than *dissolved* methylmercury in the water column.

BAFs calculated by EPA for the Savannah River largemouth bass data set range from 469,000 L/kg to over 18,400,000 L/kg. The arithmetic average of these BAFs is 4,470,000 and the geometric mean value is about 2,900,000. The standard deviation of the logarithms of these BAFs is about 0.4 units, which, when added and subtracted from the log-mean and transformed back into arithmetic space, gives a 1 standard deviation window for the distribution of these quantities ranging from 1,120,000 L/kg to 7,550,000 L/kg, a very large range. Due to the concerns mentioned above, we believe that these BAFs should be used or cited only after the most careful and critical examination.

BAFs for different species within the same trophic level may be quite different and caution should be exercised when combining data from several species. For instance, in the Savannah River, bowfin BAFs (geometric mean of 5,300,000) were nearly a factor of 2 higher than the geometric mean of largemouth bass BAFs (2,900,000). Differences of this magnitude would translate into similar differences in calculated water quality targets if those calculations were based on one species versus the other. Additionally, since many of the literature BAF values were calculated using methylmercury concentrations below the method detection limit of Method 1630, the BAF values tend to be very high. Again, due to the concerns for these data stated above, the accuracy of these BAFs is questionable.

BAFs calculated for the South Georgia Rivers included those for trophic level 3 as well as trophic level 4 fish and were based on sampling in 2000 and in 2001. BAFs for trophic level 4 fish were quite different between 2000 and 2001. Geometric mean BAFs

for trophic level 4 fish were on the order of 1,300,000 in 2000 but only 700,000 in 2001 (only trophic level 4 fish were collected in 2000 so that trophic level 3 BAFs between the two years can not be compared). The geometric mean of the trophic level 3 BAFs was 192,000 (range from 114,000 to 1,200,000) versus a trophic level 4 BAF geometric mean of 700,000 (range from 300,000 to 4,700,000). The mean ratio between trophic levels 3 and 4 in these six rivers in 2001 was 3.6. Interestingly, the highest trophic level 4 BAFs in 2000 were calculated for the Ochlockonee River (4,100,000), whereas the highest trophic level 4 BAFs in 2001 were calculated for the Suwannee River (4,800,000). In 2001, the BAF for the Ochlockonee River was only 610,000 (a factor of almost 7 difference). This analysis demonstrates the error that can arise from calculating BAFs using small data sets. It also must be noted that the BAFs calculated for the Savannah River and South Georgia rivers used total (unfiltered) methylmercury in the water column rather than dissolved (filtered) methylmercury.

Paller (2000) calculated BAFs for redbreast sunfish, predator fish (chain pickerel, longnose gar, largemouth bass, bowfin, spotted sucker and northern hogsucker), and benthic fish. Data were collected from creeks thought not to be affected by mercury point sources in and around the Savannah River Site (SRS). Unfortunately, water column concentrations (June, 1999) were not collected at the same time as the fish samples (November 1996, July and August, 1997). Water samples were from one-time sampling events. BAFs were in general lower than those reported by EPA for the Savannah River and were based on dissolved methylmercury rather than total methylmercury. Values for redbreast sunfish averaged 904,000 (range 472,000 to 1,390,000), 3,440,000 for predator fish (range 1,600,000 to 4,610,000) and 1,470,000 for benthic fish (range 786,000 to 2,220,000).

Since the BAF is not a parameter that can be predicted with any high degree of confidence, it should be measured site-specifically in order to be most useful. This in itself presents a number of difficulties, including the lack of control of a number of variables when making field measurements. In the field, one of the big disadvantages is the lack of time-averaged water column data for use with fish data, which is by its very nature time-averaged or integrated. When designing studies to measure BAFs, it is very important to understand the conditions under which the concept of a BAF is valid. To that end, the mathematical basis for the BAF is derived below. The aim is ultimately to state under what conditions the concept is valid and useful for translating from fish tissue to water column concentrations.

#### 4.2.4.2 Mathematical Basis for BAFs

Consider a simple system in which there is a constant loading rate L of a chemical to a water body. The volume of water is designated by  $V_w$  and the concentration of the chemical in the water by  $C_w$ . An organism is living in the water whose uptake rate ( $k_1$ ) is proportional to the concentration  $C_w$ . The organism biomass is  $M_o$  with chemical concentration  $C_o$ . Furthermore, the organism biomass depurates the chemical at a rate ( $k_2$ ) proportional to concentration  $C_o$ . The ordinary differential equations that describe this system are, as follows:

$$V_w \frac{dC_w}{dt} = L - k_1 C_w V_w \tag{4-1b}$$

for the water and

$$M_0 \frac{dC_0}{dt} = k_1 C_w V_w - k_2 C_0 M_0$$
(4-2)

for the organism.

The solutions to the equations are

$$C_{w} = \frac{L}{k_{1}V_{w}} (1 - e^{-k_{1}t})$$
(4-3)

for the water and

$$C_0 = \frac{L}{k_2 M_0} \left(1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2}\right)$$
(4-4)

for the organism.

The BCF (or BAF) can be defined as  $C_o/C_w$  when the system reaches steady state, that is, at large time 't'. At this time, the exponential terms approach zero and the quantity

$$\frac{C_0}{C_w} = \frac{k_1 V_w}{k_2 M_0} = BCF$$
(4-5)

Therefore, the BCF is the ratio of the organism's uptake rate to its depuration rate times the density  $M_0/V_w$  (mass per unit volume) of biomass in the water. In addition, (4-5) can be substituted into the steady-state solution for (4-4) yielding

$$C_0 = \frac{L(BCF)}{k_1 V_w} \tag{4-6}$$

Thus, we see that the concentration in the substrate dwelling organism is a function of the loading rate of the chemical to the substrate, the mass of the substrate, the uptake rate of the organism, and the BCF.

The analogies for bioconcentration of methylmercury in an aquatic organism such as phytoplankton are obvious. L is the production rate of methylmercury, dimensionally, mass per unit time. The constant  $k_1$  is the organism uptake rate (per unit time), and BCF is the bioconcentration factor (normally volume/mass). The same equations (slightly modified in their units) could easily be used to describe the bioconcentration of methylmercury in sediment, and additional equations can be written and solved analytically to describe the concentration in a higher-level predator in terms of a BAF. However, the solutions become more complicated, and challenges with the BAF approach can be pointed out as readily with the above equations.

#### 4.2.4.3 Assumptions Inherent in the Use of the BAF Approach

In the context of the models presented above, there are several assumptions inherent in the calculation and use of BAFs that can be demonstrated. The BCF (or BAF) is defined as the ratio of uptake and depuration rates and is a constant value only under steady-state conditions. At times prior to steady state, measurement of  $C_o$  and  $C_w$  would ideally underestimate the BCF. However, this may not always be the case due to other factors that may come in to play. We will discuss these factors in the context of the parameters in the model above.

#### 4.2.4.3.1 Loading Rate, L

The loading rate to the water column is analogous to the methylmercury production rate. As described above, it is a complex function of many environmental and biological factors that may vary in time and space in a water body. Some of the more important factors are geochemical controls and biological activity. Others are physical and have to do with the adsorption/desorption, precipitation/dissolution, methylation/demethylation and diffusive or advective transport from sediments to interstitial waters and to overlying waters where biological uptake occurs. Although this parameter is depicted as a constant in this model, in nature, it is varying continuously.

# 4.2.4.3.2 Uptake Rate, k<sub>1</sub>

This parameter is analogous to the rate at which methylmercury is bioconcentrated or bioaccumulated into biota. In lower trophic level organisms such as phytoplankton or periphyton, there may be a relatively quick transfer of methylmercury, and the methylmercury concentration in those organisms may be proportional to the concentration of methylmercury in the water column, although active transport mechanisms have been postulated. In higher organisms, such as fish, the uptake rate would be a function of direct uptake from the water column across gills and ingestion of mercury in prey. Gill uptake (which is considered to be a minor pathway for mercury bioaccumulation) would be a function of respiration rates and dissolved water column concentrations. Bulk ingestion rates would be coupled to the concentrations of mercury in food items. Food items change with the intricacies and dynamics of the aquatic food web and would tend to vary with season, life stage and sex of fish. Again, even though the uptake rate is depicted as a constant in the above model, it is dynamic in nature.

#### 4.2.4.3.3 Depuration Rate, k<sub>2</sub>

We are not aware of studies that have focused on the depuration rate of methylmercury in fish even though bioaccumulation is critically dependent on the rate at which a substance is eliminated. For methylmercury in fish, this rate apparently is very slow, but perhaps, not zero. For other lower trophic level aquatic life and for wildlife, the depuration rate may be greater and, therefore, of greater importance to an understanding of bioaccumulation in the food web. Most of the studies that we have reviewed in the literature have focused on tissue concentrations and not on the measurement of uptake and depuration. Study of these rates could shed some light on the bioaccumulation problem. Studying only the levels in tissue is analogous to trying to control flooding in a lake by only measuring lake levels without concurrent measurements of inflow and outflow.

# 4.2.4.3.4 Biomass Density, Mo/Vw

Biomass density has emerged as a very important consideration in the mercury bioaccumulation problem. A number of researchers have observed biomass dilution effects. That is, given the same input of mercury to a water body, levels of mercury in biota would tend to be higher in oligotrophic lakes versus eutrophic lakes because in oligotrophic lakes there is less biomass for the mercury to be partitioned into. This effect has been noted in the Florida Everglades. It also has been postulated as a reason mercury tissue levels have been observed to drop downstream of wastewater treatment plants. On a seasonal basis, biomass density may fluctuate, perhaps out of phase with fluctuations of methylmercury in the water column, which could have implications for bioaccumulation.

While these simple models are not realistic representations of the complexity of the aquatic ecosystems affected by mercury bioaccumulation, they do illustrate some of the fundamental parameters that are important to the process. Because of this feature, they may be helpful in understanding some complex issues such as conditions which are conducive to the use of BAFs, time to attain standards given reductions in mercury loadings, and the like.

# 4.2.4.4 Environmental Conditions Conducive to Use of BAFs

Ultimately, BAFs for fish can be used in two different ways, either to estimate fish tissue levels given mercury concentrations in water or to estimate water column concentrations given fish tissue levels. In either case, one should be aware of the underlying assumptions for use of BAFs, the uncertainty associated with the calculations, and implications of the use of BAFs in the regulatory context. In addition, certain types of ecological systems may be more conducive than others to the use of BAFs (i.e., match up better with the underlying assumptions described above). In cases where these assumptions underlying the use of BAFs are clearly violated in the system under study, alternatives should be considered.

Subordinate to the foregoing comment, it is most important that the variability in fish tissue concentrations and water column concentrations for mercury be understood before using BAFs for regulatory purposes (e.g., calculating tissue or water column concentrations for comparison to regulatory standards). Averaging highly variable BAFs leads to inflated estimates of the quantity because high outlier values tend to inflate the mean. We have analyzed fish tissue data from several data sets in order to quantify the variability associated with these measurements. In the Savannah River database developed by scientists at DOE's Savannah River Site, mercury in fish data spanning three years (1996 – 1998) from 12 locations (river and tributaries) for 5 species were analyzed. We found that the CV for all species at all locations was 48% (Table 4.2). When data were segregated by location (all species lumped together) and CVs calculated for each location, the CVs ranged from 34% to 53%, with an average CV of 42%. When the data were segregated by species (all locations lumped together), the CVs ranged from 32% to 42%, with an average CV of 36%. When the data were segregated by species and by location, the CVs ranged from 5% to 67% with an average CV of 30%. Thus, not unexpectedly, the variability in fish tissue concentrations is

diminished when individual species are collected and analyzed from single locations. Variability increases when data are averaged across locations, and increases even more when data are averaged across species. The greatest variability in the data occurs when multiple species are averaged across multiple locations.

Data for mercury in fish tissue were collected by EPA in the late summer of 2000 from the Savannah River. These data were collected from 12 locations in the river and tributaries (most different from the SRS locations) for 3 species (all trophic level 4 fish). Variability for all species at all locations, when aggregated, was much higher than in the SRS data, which covered a longer period and more species in multiple trophic levels. The aggregate CV for all the data was 84% (Table 4.3). CVs by location (species lumped) ranged from 23% to 86% with a mean CV of 51%. The range of CVs by species (locations lumped) was 36% to 87%, with an average CV of 57%.

Mercury in fish tissue data were collected from four locations (primarily reservoirs) in Arkansas from 1992 to 1994 (Armstrong et al 1995). The nine species collected included trophic level 3 fish (black and white crappie, bluegill, blue catfish, channel catfish) and trophic level 4 fish (black bass, largemouth bass, spotted bass and flathead catfish). As in the Savannah River data, variability for all species at all locations, when aggregated, was highest (60%) (Table 4.4). CVs by location (species lumped) ranged from 40% to 73% with a mean CV of 59%. The range of CVs by species (locations lumped) was 23% to 84%, with an average CV of 46%. When fish were segregated by species and by location, CVs ranged from 18% to 72% and the average CV was 39%.

Uncertainty in water column concentrations for methyl and total mercury are of the same order or higher. In the SRS database, the CV for total dissolved mercury (filtered samples) is 40%. The CV for total mercury in the water column (unfiltered) is higher, as would be expected, at 78%. The CV for total methylmercury (unfiltered) is still higher at 90%. In EPA's database for the Savannah River from 2000, the CVs are comparable to slightly higher. The CV for total mercury (unfiltered) is 71% and the CV for total methylmercury (unfiltered) is 107%. Data from the East Fork Poplar River, Tennessee also were analyzed (Table 4.5). These results are for the most part consistent with the other two data sets. The CV for total methylmercury (unfiltered) is 70% and the CV for dissolved methylmercury (filtered) drops to 64%. The CV for dissolved total mercury (145%), however, is greater than the CV for total mercury (60%). These data point out that the variability in water column samples is for the most part greater than that in fish tissue data. This is not surprising since fish tend to integrate concentrations in water and prey over time, which would have a dampening effect on variability.

According to error propagation theory, the percentage uncertainty in two variables is additive when they are multiplied or divided (Taylor 1982). Thus, assuming variability in fish tissue concentrations of 50% and variability in methylmercury water column concentrations of 100%, the error in the calculated BAF would be on the order of 150%. Such a wide range of uncertainty in the true value of the BAF makes comparison of a derived result for comparison to a water quality standard tenuous at best.

Given the description of the factors involved in determining the BAF from the simplistic model above, some conclusions can be drawn about the appropriateness of calculating and using BAFs in certain systems under certain conditions.

First, the analyst should be assured that methylmercury concentrations are relatively constant over time in the water column. Fluctuations in and of themselves do not prohibit the calculation and use of BAFs. The principal question is "are water column levels at a steady-state or are they fluctuating around a steady-state mean"? If they are not, then it would not be possible for the tissue concentrations in biota to be at steady state. Obviously, the smaller the organism and shorter its life cycle, the more likely it is that this condition will be met. However, since fish seem to accumulate mercury slowly over long periods of time, this is an important issue. Given declining mercury emissions and global pool of mercury, it may be difficult to find a natural system whose mercury levels are dominated by atmospheric deposition that is in steady state. On the other hand, systems, in which mercury in fish is dominated by terrestrial sources or where levels in sediments are high, may be in a relatively steady-state condition for many years, regardless of changes in atmospheric loads.

Second, the uptake rate by the organism should be relatively constant. Factors that could affect constant uptake rates would be changes in the food web of the predator or introduction of a new predator into a system. Food webs might change over time, for example, as the result of eutrophication of a lake. Reductions in nutrient levels might have similar effects, that is, to produce a long-term change in the aquatic food web. Predators may change in a system as well. For instance, the Georgia Department of Fish and Wildlife, Fisheries Management Section has documented a rise in the number of flathead catfish in the Lower Altamaha River over the past decade. During 1983 and 1984, smallmouth bass were introduced into Whatcom Lake, WA to provide a warm water fishery and have proliferated. Such changes in top-level predators in an aquatic food web would be a condition that would violate the assumptions inherent in the calculation and use of a BAF.

Systems that are relatively homogeneous spatially would be more conducive to the use of BAFs. Such a system might tend to be a small seepage lake, such as many that have been studied in the upper Midwest. On the other hand, large complex water bodies with a variety of depths and habitat types, fluctuations in water levels, and wetlands could exhibit large heterogeneity. BAFs still might be used in such systems if they could be established for species of concern within each major habitat/ecosystem type. One problem with such a system is the mobility of fish in different portions of the water body. For instance, substantial time might be spent by a largemouth bass in the wetland or tributary areas versus the main part of a large reservoir. If the bass was caught in the reservoir and a BAF calculated using relatively lower ambient methylmercury levels in the reservoir, the BAF might be biased to a higher value. In EPA's Savannah River database, it has been pointed out that fish tissue concentrations were higher by a factor of two in fish caught in the tributaries, while methylmercury levels in the water column were a factor of four higher in the tributaries.

Biomass density should be relatively constant and not changing substantially over time (constantly increasing or decreasing). If a species is undergoing a significant increase or decrease in biomass due to introduction of a new species or over management activities, the assumptions of the BAF would be violated. If young fish are introduced and growth/age produce a change of dietary habits, for instance, the onset of increased piscivory, then the BAF assumptions of a relatively constant biomass and uptake rate would be violated.

Another critical issue is the concurrent measurement of fish tissue and water column concentrations. In the past, for most of the studies where BAFs were calculated, very limited water column data have been collected. Some studies utilized by EPA to establish BAFs for use in the Mercury Study Report to Congress admittedly had single measurements or at best measurements from two seasons used in conjunction with fish of substantial longevity. Ideally, water column measurements should be made over the same period of time as the fish sampling, in seasons where suspected differences in water column or prey concentrations of methylmercury might be occurring. At a minimum, water column concentrations should be checked to insure that the data used are representative of the long-term average concentrations and that the concentrations are not trending upwards or downwards.

Finally, BAFs based on fish tissue and water column concentrations probably should not be used in systems where the bulk of the mercury load is from sediments. In such systems, the sediment methylmercury concentration is probably a better indicator of availability to fish, especially where the food chain is dominated by sediment-dwelling organisms and/or the fish of interest are bottom feeding species or species that prey primarily on organisms that derive their mercury load principally from interactions with sediments. This is to say that the fundamentals of the food web in a given aquatic system should be known before making use of the BAF concept at all. Certainly, BAFs should not be transferred, even for the same species, from one system to another unless the food web is fundamentally equivalent.

# 4.2.4.5 Spatial variability in watersheds

Spatial differences in watersheds and water bodies is a problem in determining BAFs due to the variability that may be manifested in methylmercury concentrations both in sediments, water, and biota. Obviously, if disparate results are obtained from different locations, the analyst will be faced with the problem of which data are most representative or how to combine the data to develop a representative BAF for the water body.

In the Savannah River, data indicate that fish tissue concentrations are generally higher where methylmercury concentrations in water are elevated and provide an excellent example of spatial variability of mercury concentrations in water and fish. Data from that study shows that the mean concentration in fish collected from tributaries to the Savannah River had concentrations of 0.70 mg/kg while fish collected from the mainstem were about half the tributary concentrations (0.35 mg/kg). Methylmercury was a factor of four higher in the tributaries (0.28 ng/L) than in the mainstem (0.08 ng/L). Such differences have important implications for point source dischargers on the river.

#### 4.2.4.6 Effect of Fish Size on BAF

The effect of fish size on fish tissue concentrations of mercury was discussed in Section 4.2.3.6 and the same concepts apply to the effects of fish size on the BAF. The fact that larger fish of a species have greater levels of mercury demonstrates the fact that tissue levels are not in equilibrium with uptake and depuration rates of the species. In such cases, the underlying assumption of steady state conditions for the calculation of a BAF

is violated and the BAFs are not valid. It is possible, however, that depuration rates are so close to zero in some species that they effectively accumulate mercury throughout their lives. In this case, the intake rate is the limiting factor in how much mercury their tissues will ultimately contain. It is interesting to note, however, that top-of-food-chain predatory fish rarely appear to have more than 3 to 4 ppm of mercury in their tissues. This could either be because the fish are approaching equilibrium conditions or that the availability is biogeochemically limited intake such that rarely exceeds rates that would cause concentrations on this order to be exceeded.

Is there a true BAF that is specific to a given species in certain aquatic ecosystem types or is it a mathematical construct only with little relevance to mercury bioaccumulation? At this point, we appear not to have the answer to this question. Laboratory (mesocosmtype) studies on uptake and depuration would be helpful in this regard and also would shed some light on the issue of time to attain standards.

# 4.2.4.7 Systems Dominated by Sediment-bound Mercury

Systems in which mercury in sediment dominate the loading to the water body differ substantially from those in which the loading comes predominately from water sources. In such systems, the dissolution of sediment-bound mercury or the direct uptake of sediment-bound mercury by aquatic organisms may be the limiting step in the bioaccumulation process. Uptake of inorganic and methylmercury appears to be affected by the type of substrate and the organic matter contents of the sediment.

Lawrence et al (1999) measured bioavailability of inorganic and methylmercury using digestive fluid extracted from the deposit feeding lugworm *Arenicola marina*. Methylmercury was solubilized more readily than inorganic mercury and the release from sediment inversely correlated with sediment organic matter (OM) and acid volatile sulfide (AVS) content. The authors suggest that solubilization may be the limiting step in bioaccumulation process of particle-bound methylmercury and that it is controlled by the OM/AVS content of sediments.

Wang et al (1998) measured assimilation of mercury in a marine deposit feeding polychete (*N. succinea*) from various types of sediments as well as uptake rates from dissolved phase Hg(II) and CH<sub>3</sub>Hg<sup>+</sup>. Assimilation of Hg(II) was not affected by sediment type; whereas assimilation of CH<sub>3</sub>Hg<sup>+</sup> was affected by substrate type, although sediment grain size appeared to have no effect. Dissolved uptake rate constants were twice as high for CH<sub>3</sub>Hg<sup>+</sup> as for Hg(II). Most of the accumulation of Hg(II) was predicted to be from sediment ingestion, whereas the relative uptake of CH<sub>3</sub>Hg<sup>+</sup> was dependent on the partition coefficient.

Guo et al (2001) investigated the effects of dissolved organic carbon (DOC) on the uptake of mercury by American Oysters (*C. virginica*). Metals uptake generally increased with increasing DOC concentrations; however, uptake, expressed as a dry weight concentration factor, decreased for mercury with increasing DOC. Other researchers have found that the uptake of mercury to zebra mussels increased with increasing DOC. The authors hypothesized that strong complexation of mercury with sulfur containing organic ligands may play an important role in the bioavailability and toxicity of mercury to aquatic organisms.

#### 4.2.4.8 Sediment Bioaccumulation Factors

The concept of sediment bioaccumulation factors (SBAFs) have been advanced as a means of calculating the body burden of sediment-dwelling and higher trophic level organisms from sediment concentrations. Similarly, it is possible to calculate an allowable level in sediment given standards for tissue concentrations in biota. This concept has received widespread acceptance for cleanup of contaminated sites where sediment cleanup levels are back calculated from allowable doses to receptors. Screening values (Apparent Effects Thresholds – AETs; Threshold Effects Levels – TELs: Probable Effects Levels – PELs: Upper Effects Thresholds – UETs) have been developed as indicators of sediment quality problems and have been adopted by Federal and state agencies as a means of listing or prioritizing contaminated sites for cleanup. For some organisms, partition coefficients are used as a means of predicting biotic concentrations from sediment concentrations and vice versa. In such cases the partition coefficient is analogous to a BCF, and equilibrium is hypothesized to be rapid. In higher organisms, bioconcentration or bioaccumulation is thought to be uptake limited. asymptotic to the BCF or BAF. A great deal of work has been done related to this concept in the design of bioassays to measure bioaccumulation. In particular, Corbicula are often used in tests of varying length to determine whether contaminant levels in sediments are "safe." In such cases, the SBAFs are the ratio of contaminant concentration in the organism at the end of the testing period to the concentration in the sediment.

SBAFs appear to be a function of a number of factors (US EPA 2000i), including physical (e.g., rate of sedimentation, resuspension, diffusion), chemical (e.g., redox, pH, sediment organic carbon content, sediment acid volatile sulfide content), and biological (e.g., organism size/age, lipid content, gender, organism diet). Mason and Lawrence (1999) found that the organic content of the sediments controlled concentrations of mercury in sediments, except at elevated mercury levels. The authors found no relationship between methylmercury content and acid volatile sulfides (AVS) in these sediments. They did find, however, that SBAF decreased with increasing organic carbon content of the sediments for both inorganic and methylmercury and that the SBAF for methylmercury was 2 to 50 times higher than for inorganic mercury. Laboratory studies on amphipods reported by the authors indicate that at low (<1%) and at high (>10%) sediment organic carbon, inorganic and methylmercury exhibited similar SBAFs. At intermediate values of organic carbon, SBAFs ranged from 7 to 30 for methylmercury and were approximately an order of magnitude higher than for inorganic mercury.

SBAFs measured by Lawrence et al (1999) for methylmercury in a marine lugworm were on the order of 40 (wet weight basis) at 2% organic matter and on the order of unity at OM concentrations of 10-13%.

While correlations have been found between mercury levels in sediments and sedimentdwelling organisms, most references on the subject point to little correspondence between mercury concentration in sediments and mercury bioaccumulation in fish. Mason and Lawrence (1999) found that fish tissue concentrations in Baltimore Harbor appeared to be low, despite the fact that sediment concentrations of total mercury exceeded environmental guidelines. Armstrong et al (1995) report a longitudinal increase of mercury in black bass from upstream to downstream in the Ouachita River, Arkansas. Sediment concentrations, however, are nearly constant throughout the river (<10 mg/kg), indicating that concentrations in fish do not correspond to levels in sediment. Data from EPA (2000f) in the Savannah River, Georgia, demonstrate the similar lack of relationship between mercury concentrations in fish, which increase upstream to downstream, while sediment concentrations are reasonably constant throughout the sampled length of the river. However, Cope et al (1990) found correlations between sediment mercury content and fish tissue concentration and mass. Fish tissue concentrations also were strongly correlated with lake pH and alkalinity. In general, SBAFs have not been calculated where fish are concerned. Nonetheless, SBAFs may be relevant to fish tissue concentrations in certain systems where sediment-bound mercury dominates the mercury loading to the ecosystem and where bottom-feeding fish are the species of concern.

#### 4.2.4.9 Knowledge Gaps

The foregoing discussion has pointed out a number of limitations in the scientific knowledge concerning bioaccumulation of mercury in aquatic systems. These are summarized below:

- Mechanism of uptake at trophic level 1 it appears that speciation, production of methylmercury, and uptake into biological organisms at the primary producer trophic level are fundamental to our understanding of the bioaccumulation process. At this time, there is considerable uncertainty about the mechanism of uptake by primary producers. In the past, a partition coefficient approach has been used to describe uptake at this level, while more recent research has suggested an active uptake process based on lipophilic, neutrally charged mercury species. It is essential to know how, and to what degree, methylmercury is bioaccumulated in the first trophic level, as bioaccumulation at this level appears to represent the largest increase in concentration. Biomagnification beyond this level into successive trophic levels appears to be on the order of a factor of 2 to 10. There seems to be little information on biodilution of methylmercury in systems that tend to be eutrophic rather than oligotrophic. There also seems to be little information on the kinetics of uptake at the primary producer level; that is, there is uncertainty as to whether methylmercury concentrations covary with concentrations in primary producers or whether significant lags occur between peak concentrations in water and in primary producers.
- Effect of DOC on bioaccumulation it is uncertain whether DOC inhibits or enhances bioaccumulation, although it appears that there is a net enhancement in the presence of DOC. However, at very high levels of DOC, there may be inhibitory effects. The levels at which inhibition/enhancement occur are unknown.
- Salinity effects There appears to be a definite inhibition of bioaccumulation at elevated salinity levels, associated with the concentration of chloride ion that at some level tends to result in negatively charged halomercury species. The levels at which this inhibition occurs are unknown. Therefore, prediction of bioaccumulation in estuaries is very uncertain.

- Variability among species within the same trophic level there appears to be high and unpredictable variability among individual species within the same trophic level, to the extent that mercury body burdens in some species within certain trophic levels overlap with species in adjacent trophic levels. This suggests that trophic-averaged level BAFs may be inappropriate.
- Effects of fish size on bioaccumulation age and size of fish in general would appear to be an important factor in determining tissue burdens of mercury. However, not all species exhibit strong size/body burden relationships. Therefore, it is not clear whether fish size can or should be taken into account when attempting to quantify bioaccumulation.
- Lack of information of depuration rates a good deal of information exists on levels of mercury in fish and organisms in various trophic levels. However, there is very little information on uptake and depuration rates. Information on depuration of methylmercury is essential if we are to be able to assess the length of time it will take to attain fish tissue standards if mercury loads to water bodies are reduced.
- Paucity of data for estimating bioaccumulation factors there is very little data • available for the calculation of bioaccumulation factors. Furthermore, because methylmercury values typically are at or below method detection limits, the resulting BAFs are unreliable. In addition, many of the data that have been used to calculate BAFs may not have produced reliable estimates due to violation of assumptions that underlie the BAF concept. Principally, water data have been taken in most field studies only once or twice during the course of the study and used in conjunction with fish that may have been accumulating mercury for years. Studies have indicated that water column mercury concentrations may change dramatically from season-to-season and year-to-year. Unless long-term average concentrations are used to calculate BAFs, the results may be inaccurate and misleading. Furthermore, mercury concentrations in the water column vary spatially, and field studies to date have had little control over the migration or movement of upper trophic level species. This further complicates the estimation of BAFs in natural systems.
- Lack of understanding of uptake mechanisms from sediment there is a general lack of understanding as to the effect of environmental factors on uptake of mercury from sediments. While there is general agreement on the effect of some variables on the uptake process, these effects cannot be quantified at this time.
- *Paucity of data for estimating sediment BAFs* there is a general lack of studies on the uptake of methylmercury from sediments by biota.
- Assumption of linearity of response to increasing/decreasing mercury levels in aquatic systems – perhaps the greatest impediment to establishing meaningful TMDLs for impaired waters is the lack of understanding of how increasing or decreasing loadings of inorganic mercury to aquatic systems affects fish tissue concentrations. There are numerous studies that indicate a lack of relationship between total mercury in aquatic systems and mercury bioaccumulation in fish.

This would appear to invalidate assumptions of linearity between inorganic mercury loads and fish tissue concentrations.

# 4.2.4.10 Implications of Knowledge Gaps

The foregoing discussion suggests that we are lacking some important information vis-àvis bioaccumulation in aquatic systems if we are to curtail it in certain water bodies through the implementation of regulations. We have very meager data on bioaccumulation in a limited number of water bodies. Therefore, we have *concepts* about how mercury is bioaccumulated, but we are unable to *quantify* the effect of environmental variability on that process. Therefore, we are unable to predict, with any degree of certainty, the extent to which fish will respond to increasing or decreasing loads to aquatic systems.

The establishment of TMDLs using the Agency's current approach requires that there be a translation of fish tissue concentrations to water column concentrations. To date, this has been done through the use of BAFs. There are several obstacles that severely impede our ability to make valid use of this concept. First, our lack of knowledge about the bioaccumulation process makes it impossible to calculate BAFs in one system and transfer them to others. Second, the short-term nature of studies conducted to date (in essence, the lack of long-term water quality information) makes it difficult to determine whether calculated BAFs are accurate. Third, it is not clear that any of the BAFs calculated from studies in the literature are true representations of BAFs in equilibrium conditions. If this is the case, extrapolation to other water bodies, or even use of the BAF in the water body in which it was measured, is tenuous. In such a case, we do not have a true BAF, but rather an artifact of the data, the use of which could lead to over- or under-regulation of the water body – and we do not know which. Finally, the fact that methylmercury concentrations at or below method detection limits are used to calculate BAFs makes the results extremely unreliable and uncertain - even if studies are performed under otherwise ideal conditions. Until such relationships are better understood, the calculation of water quality targets, the need for load reductions and the extent of any such reductions will be very uncertain.

# 4.2.5 Watershed Modeling and Load Calculation

EPA has made use of computerized modeling techniques to quantify mercury loading rates from nonpoint sources in a watershed. Both the watershed transport model and the water body fate and transport model used in TMDL development are empirical models, and the selection of values for various parameters in these models affects the calculated loads and the resultant water quality criterion. Various input parameters used in these models are reviewed below, and specific areas for improvements are suggested. The significance of pre-industrial/background mercury in the total mercury load to the water body, which has been discounted as insignificant in past mercury TMDLs, is highlighted with the aid of recent findings. The relative contribution of point source loads to the total mercury load in a water body is described, and suggestions are made on how to estimate loads from point source discharges.

#### 4.2.5.1 Overview of Watershed Modeling

Mercury additions to a water body generally are derived from non-point sources, such as runoff and atmospheric deposition. Point source contributions tend to be small with the potential exception of discharges from a few industries. In developing mercury TMDLs, EPA has made use of computerized modeling techniques to quantify mercury loads from non-point sources. In the Savannah River TMDL, the loading of mercury from the watershed into the river is simulated using a Watershed Characterization System (WCS) model developed by US EPA Region 4 (US EPA 2001c), which provides a simplified simulation of precipitation-driven runoff and sediment delivery. This has been combined with "The Mercury Tool," an extension of the Arc-View based WCS model used to simulate mercury transport in the watershed derived from algorithms in the Mercury Study Report to Congress. The solids load from runoff is used to estimate pollutant delivery to the receiving water body from the watershed. This estimate is based on mercury concentrations in wet and dry deposition, which is modified by contact with watershed soils and ultimately delivered to receiving water body by runoff, erosion and direct deposition. The WCS model has been used in tandem with the Water Quality Analysis and Simulation Program (WASP5) (Ambrose et al., 1993), which simulates the fate and transport of mercury in the aquatic system. The model output was calibrated using site-specific measurements of mercury and methylmercury in water, sediments, and soils. A number of key assumptions that go into these models are evaluated below. However, an important assumption is that recently deposited atmospheric mercury provides the overwhelming majority of inputs to the watershed – other older anthropogenic sources and naturally occurring sources are disregarded. We consider this to be a fundamental flaw in the algorithms and the application of this model.

#### 4.2.5.2 Estimation of Wet/Dry Deposition

The WCS mercury model uses input of the appropriate wet and dry deposition rates for mercury. Both measured values from the Mercury Deposition Network (MDN) and extrapolated from RELMAP air deposition model results reported in the Mercury Study Report to Congress have been used. These two sources have very different wet and dry deposition rates for a given location (US EPA 2000j), and EPA has been inconsistent in its use of them. While EPA dismissed the RELMAP deposition estimates in the South Georgia TMDLs (US EPA 2001f) as being "based upon an outdated emissions inventory and did not include other foreign sources," RELMAP model output was used for the Savannah River TMDL (US EPA 2000f). Since atmospheric depositional rates can vary widely between watersheds, it is recommended that a critical review of these two sources be conducted to select the one best representative of depositional rates. If monitoring stations are available within a watershed, average annual rates of wet and dry deposition from the monitoring station should be used in lieu of other data or estimates.

# 4.2.5.3 Estimation of Mercury Reduction in Soils

Recent national mercury emissions inventories estimate that re-emission of previously deposited mercury from soils, sediments, water, and aquatic and terrestrial vegetation is similar in magnitude to on-going industrial emissions. The quantity of mercury re-

emitted from terrestrial environments is poorly known. Mercury can be re-emitted from terrestrial environments through vegetation or through direct loss from soils. Mercury volatilization from soils is influenced by moisture content of the soil, organic matter content in soil, light penetration, sunlight intensity, wind velocity, and many other factors. Vegetation also plays an important role in mercury loss, where the volatilized mercury may be derived from soils (plant uptake and transpiration) or from the mercury deposited on leaves in the form of wet and dry deposition. The role of vegetation in mercury loss also is not well understood, nor is the significance of re-emission sources from terrestrial environments.

In the WCS model, volatilization loss of mercury is calculated by a purely empirical equation that uses a reduction loss rate constant, soil base reduction rate, and a soil reduction depth. Choice of these rates can alter significantly the mercury balance in the watershed since volatilization and the choice of "default" values used in EPA's previous model runs may result in large biases in the estimated mercury loads.

# 4.2.5.4 Estimation of Watershed Transport

Mercury deposition rates to the watershed, estimated from the RELMAP or MDN data, are converted to GIS coverage to provide a spatially variable deposition rate for the watershed (Ref: Savannah River TMDL). The Mercury Tool of the WCS model (US EPA 2000h) is used to calculate the mercury mass balance in the soil and the total load of mercury entering the main stem portion of the river. For each of the sub basins, the percentage of the contribution from soil erosion, runoff, direct deposition, and impervious soils are separately calculated, and the watershed model is calibrated to match the soil concentrations measured in the field. A number of assumptions go into modeling how much of the mercury deposited from atmospheric sources is transported from the watershed to the water body. Some of these key assumptions are reviewed here.

#### Soil Mercury in Water and Solid Fraction at Equilibrium:

The equation as shown in the model (US EPA 2000h) represents mercury partitioning in soil as a simple equilibrium process. While there may be equilibrium partitioning of some ionic forms of mercury (divalent and methyl), other forms of mercury may not exhibit true equilibrium in soils. Inorganic mercury may be complexed as cinnabar or meta-cinnabar under reducing conditions in flooded soils, such as may occur in wetlands and low-lying areas, and become unavailable for methylation or export to the water body. Additionally, the partition coefficient,  $K_d$ , for mercury varies over several orders of magnitude for soils (depending on the soil type, organic matter content, grain size, etc.). Using a single  $K_d$  value for the entire watershed may introduce a large bias in the model results. Biases also could be introduced from the choice of values for porosity, bulk density, and soil moisture content. Sensitivity analyses have not been conducted on the significance of these parameters.

#### Calculation of Mercury Loss Rate Constant:

In WCS, mercury loss from watershed soil is related inversely to the depth in soil profile to which mercury is incorporated (referred to as the mixing depth,  $z_d$ ), the choice of which can dictate the loads generated from the watershed. Past model runs (e.g., Savannah River TMDL) have assumed a mixing depth of 2 cm for untilled soil, which is very shallow. Adriano (1986) shows an example of mercury in a soil profile in a podzolic soil developed under a beech forest where concentrations of mercury exceed 50 ng/g to

a depth of 30 cm, then decrease substantially. This can be explained by the complexation of mercury by DOC in the infiltrating groundwater. Earthworms, which are frequently observed from 0-30 cm in soils, can also mix the pollutants in the topsoil to depths greater than 2 cm. More recent evidence suggests that mercury in three untilled soil profiles in South Georgia is nearly constant in the top 15-20 cm of the soil profile (AMEC, 2002, unpublished data).

Because mercury loss is indirectly proportional to the mixing depth in WCS, increasing the mixing depth from 1 cm to 20 cm, for example, would reduce the calculated total mercury concentration in soil from 126 ng/g to 14 ng/g in the example provided by EPA (US EPA 2000h). Thus, a small mixing depth can result in unrealistically high export rates (loads). It is strongly recommended that WCS model runs include site-specific soil mercury concentrations and soil mixing depths so that a reasonable export rates can be calculated.

# Mercury from Pre-Industrial/Background Sources:

In mercury TMDL models, it has been assumed that most of the mercury in the watershed (and water body) is of recent atmospheric origin, and that there is a substantial buildup of this "recent" mercury in the top few centimeters of the soil. In reality, mercury concentration data in soil cores are few, and no attempt has been made to determine the relative significance of mercury from background sources (i.e., mercury associated with soil from the weathering processes as well as mercury deposited during pre-industrial times).

The significance of background soils concentration can also be illustrated from the Savannah River data. Based on the soils data collected by EPA from the Savannah River basin, the average concentration of soils samples is 58.7 ng/g (incidentally, this concentration is comparable to average crustal abundance). Adriano (1986) reports that the earth's crust contains an average of 50 ng/g and that soils may be considered normal if their mercury contents are below 100 ng/g. Assuming a bulk density of 1.3 g/cm<sup>3</sup>, the total mass of mercury in the top 20 cm of the Savannah watershed soil is calculated as 15,262  $\mu$ g/m<sup>2</sup>. Even with a conservative atmospheric depositional rate of 18  $\mu$ g/m<sup>2</sup>/yr, an estimated 848 years of deposition would be required to account for this much mercury in soil. This is a conservative estimate since the depositional rates could have been much lower during pre-industrial times. Thus, a large portion of this mercury in soil must have been derived from pre-industrial and/or background sources. We strongly recommend that a more realistic "background" soil mercury concentration (C<sub>0</sub>), based on site-specific measurements from deep soils, be included in future applications of WCS.

# Calculation of Mercury Erosion Load:

In the mercury tool of the WCS model, erosional losses are calculated based on the empirical Universal Soil Loss Equation (USLE). Selection of improper values for any of these empirical factors could dictate the results of the simulation. The mercury erosion load calculation assumes that all erosion is sheet erosion of the top layers of soil, presumably over the entire watershed or sub-watershed area. This is a major flaw in the model because erosion typically does not occur as sheet erosion over large areas, and the top centimeter of the entire forested area, for instance, does not contribute to sediment mercury load. Only a small fraction of the entire watershed area typically makes a substantial contribution to the erosion load, except perhaps in areas consisting of leveled, cultivated fields. Significant sources of erosion are rills and gullies, which

contribute sediments derived from soils deeper in the profile. Sediments from these sources (e.g. stream banks) may contain a predominance of pre-industrially derived mercury.

The Savannah River TMDL WCS modeling neglected other terrestrial sources of mercury. Consequently, a very high rate of loss (through erosion and runoff) had to be simulated in order to calibrate the model output runs to observed concentrations in water (i.e., about 32% of mercury deposited annually was required to be transported into the river in model simulations to match observed concentrations in the river). Such a high export rate is highly unlikely because other particle-reactive contaminants are washed off much more slowly (for example, plutonium, which has  $K_d$  values similar to mercury, is exported at a rate of ~0.02% per year from watersheds (Ravichandran et al 1995). Preliminary evidence for slow removal of recent mercury from watersheds is emerging from the METAALICUS project underway in the Experimental Lakes Area (ELA) in Ontario, Canada. Of the entire quantity of stable mercury isotopes added to the upland catchment area at ELA, only about 0.3% were exported during the first year (Phase I), and most of the other mercury that was exported was old mercury which had been accumulating in the soils for many years (Harris et al., 2001). The isotopic mercury also was much more mobile, penetrating into the 10-20 cm below the peat surface.

The WCS model does not account for transport of mercury to water bodies other than overland flow and erosion. Thus, leaching to shallow groundwater and reentry of mercury into surface streams via this transport mechanism is overlooked. Krabbenhoft et al (1995) showed that mercury in shallow groundwater discharges through peat wetlands contributed significantly to mercury export from the Allequash watershed in northern Wisconsin. Mercury in shallow groundwater discharges could be derived from a mixture of recently deposited atmospheric sources, older anthropogenic sources, and naturally occurring sources.

#### Model Calibrations:

As mentioned earlier, WCS/WASP simulated model outputs for different computational segments of the stream were calibrated with field-measured concentrations of total and methylmercury in water and sediments. Review of the modeling output from the Savannah River TMDL shows that the models did not predict the concentration of mercury in sediments and methylmercury concentrations in water or sediments well (see figures below; taken from Savannah River TMDL Administrative Record).

While the simulated mercury concentrations in sediments appear to be increasing in the downstream direction, the observed data exhibits no such trend. The over-simulation of sediment and water concentrations near the river mouth is crucial because it is in these segments that EPA ultimately calculated the load reduction required to meet the water quality target of 2.8 ng/L.

#### 4.2.5.5 Estimation of Aquatic Fate

In developing the mercury TMDL in the Savannah River, EPA combined models of watershed loading of mercury (WCS model with Mercury Tool) with a model of mercury cycling in the receiving water body. WASP5 was chosen to simulate mercury fate in these water bodies. WASP5 is a general dynamic mass balance framework for

modeling contaminant fate and transport in surface waters. Each chemical exists as a neutral



**Total Hg Concentration in Sediments - Annual Average Flow** 

Figure 4-5. Comparison of observed and simulated mercury in sediments under average annual flow conditions, Savannah River, GA (Source: US EPA 2000f)



Figure 4-6. Comparison of observed and simulated water column methylmercury in the Savannah River, GA (Source: US EPA 2000f)

compound and up to four ionic species; and the neutral and ionic species can exist in five phases: dissolved, sorbed to dissolved organic carbon, and sorbed to each of the three types of solids. A number of reactions are modeled in this model, including the

partitioning of mercury to various types of sediments and dissolved organic carbon, oxidation of elemental mercury in water to Hg(II), reduction and methylation of Hg(II) in the water column and sediment layer, demethylation of methylmercury in water column and sediment layer, and volatilization of elemental mercury from water surface.

Modeling these reactions requires input of various coefficients and rates, many of which are not readily available or easily measured. Because most of these values are taken from literature, and these values can vary by orders of magnitude between different aquatic systems (or vary spatially and temporally within the same water body), inaccurate simulation of the system may result. For example, partitioning of mercury to organic matter and sediments can change as a function of pH, sediment grain size and properties of adsorption surfaces; methylation and demethylation can change diurnally or seasonally depending on microbial activity, organic matter concentration, redox, and other parameters; and oxidation and reduction of elemental and ionic mercury may be modified by organic matter, microbial activity, and sunlight intensity. Given these uncertainties, the selection of literature values should be made carefully and model results viewed with caution.

#### 4.2.5.6 Development of Load

The above-mentioned limitations in the watershed loading model (WCS) and the receiving water body fate and transport model (WASP5) make estimates of mercury loads in previous TMDLs unreliable. While we agree that the model calculations will almost always have inherent limitations and may never completely match field conditions, we stress the importance of careful selection of input parameters for these models. For example, as described earlier, changes in mixing depth for atmospherically derived mercury in soil and changes in adsorption coefficients to soil (K<sub>d</sub>) alone could affect the estimated load by a factor of about 10 in Savannah River (in this case, lower the estimated total load). Lacking reliable estimates of background loads, the relative significance of recent atmospheric and point source loads cannot be adequately determined. Therefore, load allocations cannot be assigned.

# 4.2.5.7 Knowledge Gaps

Both the WCS model used to estimate the nonpoint source load from the watershed and the WASP5 model used to estimate fate and transport of mercury in the receiving water body are empirical models and require the input of a number of parameters and assumptions. Many of these parameters are selected from the literature because it is impractical to measure them for each water body and watershed. This introduces uncertainty in the model estimates of nonpoint source loads. Estimates of dry and wet deposition can be very different between the two primary sources of information (MDN data and RELMAP model output), and extrapolated atmospheric deposition rates should be verified carefully against any monitoring data available for the watershed under study.

Large uncertainties also are introduced in the nonpoint source loads estimated for the watershed due to the choice of various model parameters in the WCS model. For example, assumptions made in previous use of these models for mercury TMDLs could easily have introduced bias in estimated loads by a factor of 10 or more. Combined with

the spatial and temporal variability in other environmental processes (such as adsorption of mercury to solids or DOC) and our inability to predict methylation in the environment accurately, it is no surprise that these models poorly predict field-measured concentrations of mercury and methylmercury, as illustrated earlier.

# 4.2.5.8 Implications of Knowledge Gaps

Mercury loadings to a water body result from several categories of sources including currently existing anthropogenic air sources, natural air emissions, older anthropogenic air emissions/sources no longer subject to control, natural sources from within the watershed (i.e. weathering of soils and rocks), and to a small degree, point sources. Given the lack of knowledge concerning the export rate of mercury from watersheds to water bodies and the relative contribution of older anthropogenic and natural background versus more recent anthropogenic sources, it cannot be concluded whether, or the extent to which, these other sources are significant relative to existing air sources. Mercury derived from pre-industrial sources and naturally occurring background mercury in soils may contribute significantly to the total mercury load in a water body in systems where fluvial processes dominate loading.

Air emission controls will impact only new additions of mercury. Furthermore, methylmercury production in the water body from inorganic mercury additions may be limited by environmental factors such as sulfate and DOC. Perhaps the best example of this is Lake Superior, where new additions by air are small compared to historic additions from a century and a half of mining and milling. As a result, it may take much longer for large watersheds to respond than EPA's modeling efforts would suggest. Various assumptions used in WCS and WASP models need to be reevaluated, and appropriate site-specific and reasonable parameters must be included in these models in order to estimate current mercury loads, time to attain standards, and the load reductions required to attain standards.

4.3 Recommended Improvements for Control of Mercury Under the Clean Water Act (CWA)

In this section we make recommendations for improvements to the implementation process. The discussion centers on recommendations regarding the deficiencies in existing approaches and data vis-à-vis the knowledge gaps identified in previous sections.

#### 4.3.1 TMDL Development

#### 4.3.1.1 Improvements to Better Account for the Methylation Process

EPA's approach for calculating a mercury water quality target for the protection of human health currently makes the simple assumption that methylmercury is a constant proportion of total mercury in the water column. As discussed previously, methylmercury production in aquatic systems is not a simple function of total mercury concentration in the system, but is rather influenced by a number of complex, often inter-related, factors. Unfortunately, solutions to methylmercury problems in fish are largely centered on reducing total mercury additions to the water bodies, even though the preponderance of studies has suggested that methylmercury production is rarely a function of total mercury in the system. Each environment responds uniquely to mercury methylation, and currently, there are no models available that can be used to reliably predict methylation rates in aquatic systems. Due to the complex interplay of biogeochemical processes involved, it may be a long time before such predictive models become available.

Past studies have indicated that measuring certain important environmental parameters (e.g., pH, redox) can shed light on the factors that enhance or inhibit methylmercury production in a single water body or at a regional scale (e.g., seepage lakes in Wisconsin). Generally, microbially mediated methylation is favored under anaerobic conditions, while demethylation is favored under aerobic conditions. In the water column, methylmercury production is related to zones of low oxygen concentrations, and methylmercury concentrations are highest at the oxic-anoxic boundaries of stratified lakes and estuaries. Lateral and vertical differences in redox state within a water body can help explain some of the differences in methylmercury concentrations, in the water column and sediments, and it is important to measure the spatial and temporal changes in redox state within the impaired water body as part of TMDL sampling. Sulfur chemistry is another important parameter that substantially determines methylation rates in many aquatic systems and needs to be quantified in TMDL development.

Organic matter concentration (measured as dissolved organic carbon in water, or as total organic carbon in sediments) is another important parameter in mercury methylation. High organic matter stimulates bacterial activity, favors anoxia, reduces light penetration, and forms complexes with mercury and methylmercury. Methylation can be enhanced or inhibited by organic matter, depending on the concentration and chemical properties of the organic matter. It can be hypothesized that the relatively labile (low-molecular weight) organic matter in water and sediments stimulates bacterial growth and methylation, while the refractory organic matter (humic and fulvic acids) complexes with mercury and makes it less bioavailable for methylation. DOC concentrations normalized to UV absorbance (at 254 nm or other suitable wavelength) may be a very useful, yet relatively easy and inexpensive, way to determine whether the organic matter might enhance or inhibit methylation.

Therefore, in addition to the sampling and analysis of methylmercury in a given water body, sampling for TMDL development should include measurements of the following geochemical parameters in water: temperature, pH, redox, sulfate, sulfide, and dissolved or total organic carbon. Analysis of these ancillary parameters may not only aid the interpretation of methylmercury data in a given water body, but also may contribute to the understanding of methylation processes in general and the future development of valid predictive models.

#### 4.3.1.2 Improvements to the BAF Approach

As discussed above, key areas in which scientific knowledge is lacking which prevents the calculation and realistic use of BAFs for the purpose of translating a fish tissue-based criterion to a water column-based criterion for use in TMDLs are, as follows:

- mechanism of uptake from water into lower trophic level organisms;
- effects of environmental variables (e.g. DOC, pH, salinity) on bioaccumulation;
- effects of fish size on bioaccumulation;
- accurate estimation of depuration rates;
- lack of quality data (especially concurrent fish tissue and long-term data for mercury in the water column);
- mechanism of uptake from sediments into lower trophic level organisms; and
- linearity of response to lowering inorganic mercury loads.

If EPA intends to continue promoting the use of its linear formula for calculating water column "criteria" intended to be protective of human health from consumption of fish, a great deal of progress could and should be made by conducting studies in a comprehensive manner that address these issues. These studies should be combined with laboratory/modeling and field evaluation projects. For instance, laboratory mesocosm studies could be conducted to study food chain biomagnification of methylmercury in the presence of varying levels of DOC, pH, salinity or other environmental factors. Based upon the results, models would be constructed. These models would then be tested by acquiring field data and determining how well the models are able to predict results.

Until such research is done, we believe it is premature to attempt to translate from a fish tissue-based criterion to a water-column-based criterion. The regulatory implication of this conclusion is that comprehensive TMDLs may not be feasible for decades, considering the time necessary to achieve the technological improvements identified earlier and the time necessary to collect the site-specific information necessary to develop these improvements.

In the interim, in addition to advancing the overall state-of-the-science required for the technically defensible regulation of mercury, we recommend the following steps:

- where TMDLs are required (e.g., by court order) before necessary information is available, use a phased TMDL approach;
- water column-based water quality standards should not be calculated or set in the initial phases of a phased TMDL or a pre-TMDL permit procedure;
- load reductions should not be imposed upon point sources in the first stages of a phased TMDL or a pre-TMDL permit proceeding, unless there is ample evidence that the point source is causing an excursion of a state water quality standard for mercury;
- load reductions should not be allocated to point or nonpoint source loads until such time as a linkage can be established between an emission or discharge and a water quality impairment; deposition or discharge of inorganic mercury into a water body in trace quantities does not establish such a linkage;
- monitoring plans should be established in phased TMDLs in order to attempt to determine the linkage between loads and water quality impairments;
- monitoring plans should be developed and implemented to establish water quality trends; and
- monitoring plans should be developed and implemented in order to identify the relationship between load reduction and ecosystem (especially fish) response.
In systems where fluvial processes (i.e., runoff and erosion) dominate loadings to the water body, TMDLs should focus initially on the collection of data to identify the amount of mercury contributed by atmospheric, terrestrial (anthropogenic or natural background) and point sources. Without such information for a given watershed, it will be impossible to establish realistically the required load reductions, allocate load reductions, or estimate the time frame required to attain the standard.

If EPA or the states decide to base a TMDL on a water-column-based criteria (derived from a fish tissue criterion or the RfD) as part of the process, then we recommend that a model with some degree of scientific sophistication, such as EPRI's Mercury Cycling Model, be used to model aquatic fate and biological uptake. It is not recommended that simple models utilizing BAF or SBAF concepts be used to derive water column-based criteria from fish tissue-based criteria, unless the quantities are estimated using reliable data bases developed using the following:

- site-specific studies of 3-5 year duration should be conducted to establish BAFs;
- a sampling plan along the lines presented in this document should be developed and implemented; and
- research should confirm that none of the assumptions underlying the use of the BAF concept have been violated.

Also, an accurate creel survey of the water body should be conducted to support an assessment of fish caught and consumed (quantity and species) from the water body. The resulting BAFs calculated from such studies should be weighted by trophic level or by species caught and consumed in order to set water quality targets.

While weighting by trophic level, as was done in establishing the methylmercury criterion, is a step in the right direction, weighting by specific species caught and consumed is preferable due to the variability of mercury tissue burdens among species in the same trophic level. Appendix B contains an example calculation, excerpted from comments to the Savannah River TMDL provided to the EPA by the Georgia Power Company, that demonstrates the importance of utilizing weighted BAFs. In this example, the use of a weighted BAF versus a "trophic level 4 only" BAF vields a water quality target that is over a factor of two higher than EPA's calculated water quality target. The relevance of this difference is that the total mercury in the water column in this system appears to be biogeochemically controlled at about 3 ng/L. The water quality target calculated by EPA Region 4 is under this level (2.8 ng/L), while the water quality target calculated as a result of weighting the BAF is over this level (6.9 ng/L). This higher target level is consistent with the argument that the beneficial use of fishing in Savannah River is not impaired and with the recent decision of the Georgia EPD to remove the Savannah River segments from its § 303(d) list. Segments were proposed for removal from the list after the State of Georgia adopted EPA's new methylmercury criterion and subsequently reanalyzed fish tissue data in view of the assumptions that underlie the use of the criterion.

In addition, it is important that the data be analyzed so that error and bias are minimized in resulting calculations. Analysis of the Savannah River fish tissue data collected by EPA Region 4 reveals some important points in this regard, as discussed below in the following paragraphs. None of the analytical methods for methylmercury have been validated in an interlaboratory study performed in accordance with ASTM or equivalent procedures. Thus, much uncertainty remains regarding the reliability of methylmercury data and its reproducibility within and between laboratories. This is a fundamental shortcoming in the mercury regulatory process that EPA should eliminate.

Unfiltered total and methylmercury water column and fish tissue data were collected from sixteen locations. While concentrations in fish tissue data averaged 0.482 mg/kg overall and the coefficient of variation (CV) was 69% for fish composites, water column methylmercury averaged 0.15 ng/L with a CV of 102%. Calculated BAFs averaged 4.6 x 10<sup>6</sup> with a CV of 70%. Thus the variability of the BAFs was about equal to that of the least variable of the two factors that make it up, the fish tissue data. These data have a linear correlation coefficient (r) of about 0.53. The probability that the correlation coefficient would exceed 0.5 if these two variables are uncorrelated is 4.9%, indicating *significant* evidence of linear correlation. We would expect the CV of the quotient to be lower in this case since high values of methylmercury in the water column tend to be associated with high values in fish tissue and vice versa; thus the uncertainty in the quotient tends to be lower.

Total mercury in the water column averaged 3.44 ng/L with a CV of 67%. The fraction methylmercury calculation (methylmercury in the water column divided by total mercury in the water column) averaged 6.49% with a CV of 96%. Therefore, in this case the CV of the quotient was about equal to the more variable of the two factors, methylmercury in the water column. The correlation coefficient between these two variables is close to zero (r = -0.146), indicating no significant evidence of linear correlation (Taylor, 1982). The lack of correlation in these two variables yields situations where low values of total mercury in the water column; thus the variability in the quotient tends to be higher as indicated by the higher CV (the spread in the calculated results).

Interestingly, in contrast to the average calculated from the BAFs from the sixteen locations  $(4.6 \times 10^6)$ , the BAF produced by averaging the fish tissue data and water column methylmercury data and dividing is substantially lower  $(3.1 \times 10^6)$  and close to the geometric mean of the BAFs for the sixteen locations  $(3.45 \times 10^6)$ . The same holds true for the calculation of the percent methylmercury. In contrast to the average calculated from the sixteen water column methylmercury data points (6.49%), the percent methylmercury produced by averaging the methyl and total mercury data and dividing these two averages is substantially lower (4.5%) and close to the geometric mean of the calculated percentages of methylmercury (4.23%).

This analysis demonstrates the bias that enters the calculation of the water quality target when arithmetic averages are used to calculate the BAF and percent methylmercury quantities. The CV of the quotient is exaggerated due to the influence of data pairs where high values of one variable are associated with low values of the other variable. This effect is reduced when the two variables are correlated. The use of the geometric mean of the calculated BAFs and percent methylmercury (which also mitigates the influence of higher values) seems to give a result that is more consistent with the result produced by averaging beforehand the two variables that form the quotient.

By this same logic, reducing the number of calculations contributing to the propagation of error in the result is appropriate. By using an arithmetic average BAF and arithmetic

average percent methylmercury, a low water quality target of 1.34 ng/L is derived. If one of these calculations is eliminated (that is, by using an arithmetic average BAF based on total rather than methylmercury where the use of the methylmercury percentage in the calculation is avoided), the resulting water quality target is higher (2.85 ng/L). If the water quality target is based on geometric means of the BAFs and percentage methylmercury, the calculated water quality target is similar to the latter result (2.75 ng/L).

It is important that the analyst realize that the use, in this instance, of arithmetic means where quotients or products are being calculated produces a bias in the result. In this case, where the BAFs and percentage methylmercury are inflated and are in the denominator of the equation for the water quality target, that bias tends to drive the water quality target downward. Even though there is no relationship between total mercury in the water column and fish tissue concentration in this data set, it is perhaps more appropriate to use a BAF based on total mercury because of the propagation of error and the resulting bias in the result. A similar effect appears to be achieved by using geometric means for BAF and percent methylmercury in the calculations.

# 4.3.1.3 Improvements in Sampling

From the foregoing discussions on mercury sampling and analysis, it is obvious that the final water quality criterion and the load allocation can be significantly affected by the way the mercury and methylmercury sampling is conducted in different environmental media. A number of factors need to be considered in devising a sampling plan for the analysis of mercury and methylmercury and other environmental parameters. Some of the important ones include the following:

- the size of the water body and watershed;
- heterogeneities within the water body/watershed;
- presence of any significant point or nonpoint source (such as mine drainage or contaminated sediment from mine site);
- seasonal variations in mercury loadings;
- daily and seasonal changes in methylmercury production and loadings;
- spatial variations in mercury and methylmercury in fish, sediment, and water; and
- changes in key environmental parameters (such as temperature, pH, redox, sulfate, sulfide, dissolved organic matter).

An important missing element in past TMDL sampling is consideration given to the food web structure that supports the fish populations, which plays a vital role in determining the mercury concentrations in fish (Section 4.2.2). For example, mercury methylation may be predominant in the water column in some ecosystems and in sediments in others. Depending on whether the primary source of exposure is from sediment-dwelling organisms or from organisms living in the water column, mercury levels in fish can be very different. Since the feeding habits and food web structure vary considerably between different aquatic ecosystems, a careful evaluation of the food web is necessary to determine what type of sources (i.e., water, air, sediment) needs to be controlled in order to reduce mercury levels in fish.

Another source of concern arises from the determination of mercury and methylmercury concentrations in unfiltered water samples, as has been done in recent TMDLs (e.g., Savannah River TMDL). While it is true that most of the mercury and methylmercury load is associated with sediments, determination of the water quality criterion should be based on filtered (i.e., dissolved) water samples because BAF values are calculated based on "dissolved" methylmercury concentrations in water, not "total" methylmercury concentrations. Seasonal variations also are very large for unfiltered water samples (due to changes in suspended particulate load which are a function of rainfall, runoff. erosion etc) and introduce large uncertainties in sampling results. Additionally, if unfiltered water samples are used to set the criterion, it will be difficult to assign loads to point source discharges due to seasonal fluctuations in the intake water, and dischargers potentially will have to use unfiltered samples in assessing compliance to the standard (some of the sediment load may be removed within the plant for specific applications). We strongly recommend that filtered water samples be used for mercury and methylmercury analysis in order to minimize seasonal variations associated with sediment-associated mercury.

Different water bodies (lakes, streams, and estuaries) exhibit different methylation efficiency and support different aquatic habitat, and this should be reflected in the aquatic sampling plan (i.e., sampling plan for a lake should be different from that of a stream). For purposes of sampling plan development, water bodies can be divided into five types, as follows:

- well-mixed lakes;
- stratified lakes;
- streams and rivers;
- wetlands; and
- estuaries.

Some sampling issues are applicable to all aquatic systems, while there are other issues that are unique to each of these aquatic systems. A primary differentiator in the sampling strategies for these different water bodies is whether the aquatic food web is periphyton-based or plankton-based. It should be noted that this report is not intended as a comprehensive guide for mercury sampling for each and every type of watershed, but rather provides some general guidelines and recommendations for minimizing spatial and temporal variability in methylation and bioavailability.

#### 4.3.1.3.1 Common Sampling Issues

<u>Spatial Variations and Sampling Intensity</u>: As discussed earlier, mercury and methylmercury concentrations can vary substantially in different parts of the watershed. For example, total mercury concentrations can be substantially different between the tributaries and the main stem of rivers due to different loadings in the watershed. Methylmercury concentrations can vary with depth within a lake (depending on the presence and location of the hypolimnion, changes in redox and organic matter concentration, etc.) or in an estuary due to changes in salinity and sulfate reduction. Where there is considerable variation in methylation efficiency within a watershed, as observed between the tributaries and the main stem of the Savannah River, it may be appropriate to develop water quality criterion for individual sections of the watershed (e.g., tributaries), rather than the whole system. Sampling intensity and locations should be selected based on the size of the watershed and the heterogeneity in methylation, mercury load, and food web structure, among other factors.

<u>Temporal Variations and Sampling Intensity</u>: As described previously, seasonal changes in total mercury concentrations, and diurnal and seasonal changes in methylmercury concentrations can significantly affect the calculated water quality criterion. As observed from the South Georgia TMDLs, one-time sampling of water bodies can be very misleading, is inadequate, and should not be used to establish a criterion. Seasonal changes in total mercury can occur in streams and rivers due to changes in runoff, and in lakes due to changes in wet and dry deposition as a function of precipitation. In streams and rivers, sampling should be repeated at different times of the year (e.g., spring runoff, low summer flow) to capture seasonal variability in mercury loads and methylmercury production. For lakes, temporal variability should be addressed by sampling during different times of primary productivity, changes in hypolimnion, and changes in mercury loads from drainage/atmospheric sources, among others. A minimum of three sampling periods is recommended to address temporal variations in the water column and sediments.

<u>Sampling of Environmental Parameters</u>: While the process of methylation and bioaccumulation are poorly understood, measuring key environmental parameters can shed light on processes that favor methylation and bioaccumulation and help explain spatial and/or temporal variability in methylmercury concentration within a given system. In addition to measuring mercury and methylmercury in sediments and water, the following parameters also should be measured: pH, temperature, DOC, sulfate, sulfide, and redox potential, in addition to other site-specific parameters that may be warranted in different ecosystems.

<u>Food Web Structure</u>: The feeding habits for fish are very different for different species, and the fish tissue mercury levels can be influenced significantly by the feeding habits. Mason et al (2001) note that most of the mercury enrichment takes place in the lower trophic level, with the zooplankton exhibiting a BAF of about 10<sup>5</sup>, and only a slight increase in BAF from zooplankton to fish (on the order of 10<sup>6</sup>). In addition to measuring mercury levels in fish tissue, it is also recommended that the fish gut contents be examined for prey items. If the fish are feeding on smaller fish, it may be necessary to examine the gut contents of the prey fish as well. This can shed light on whether the primary route of exposure is from sediments (through the ingestion of benthic invertebrates) or from water (through the ingestion of phytoplankton/zooplankton).

<u>Source of Mercury</u>: Careful consideration should be given to the predominant source of mercury in the watershed for which a water quality criterion is being developed. In water bodies with a large surface area and little or no drainage, the primary source of mercury may be atmospheric. In such cases, reduction in atmospheric mercury loading might lead more readily to reductions of mercury levels in fish. In systems that receive mine drainage, the primary source of mercury may be mercury-contaminated sediments. In cases where the primary route of exposure is from sediments, it may be because the sediments are grossly contaminated with inorganic mercury, and that the bottom feeders are ingesting mercury-contaminated sediments and passing it up the food chain. No attempt has been made in the past to determine whether mercury in fish in such systems might be primarily in the inorganic form (inorganic mercury is much less toxic and is depurated at different rates than methylmercury). In those water bodies, it may be

necessary to consider management options for mercury-contaminated sediments. On the other hand, if the mercury concentrations in sediments are within "normal" levels, and high mercury levels in fish are a result of higher methylation rates (due to sitespecific biogeochemical conditions that favor methylation), sediment management would not be a viable solution.

## 4.3.1.3.2 Sampling in various types of water bodies

<u>Well-Mixed Lakes</u>: In lakes that are well mixed, mercury concentrations may be expected to be uniform in the water column; and depending on the redox conditions and other biogeochemical factors, methylation may be largely confined to the sediment-water interface. In these lakes, the primary food web may be either phytoplankton-based or periphyton- based and this can affect mercury accumulation in fish. Additionally, the total and methylmercury concentrations can exhibit seasonal variability depending on whether the lake is a seepage lake (i.e., water derived from groundwater and rainfall) or a drainage lake (water mostly derived from terrestrial runoff), which needs to be considered in devising a sampling plan.

<u>Stratified Lakes</u>: Lakes that have distinct hypolimnion can be expected to show large gradients in primary productivity, DOC concentrations, redox, temperature, sulfide production, and other factors all of which exert strong influence on methylmercury production and bioaccumulation. These lakes may exhibit strong seasonal variability in mercury cycling and methylmercury production, both within the water column as well as at the sediment water interface. As illustrated by Hudson et al (1994) and Hurley et al (1994), mercury cycling in stratified lakes can be quite complex and it is important to collect samples during different seasons and at different depths in the water column

<u>Wetlands</u>: While the wetlands themselves may not be listed as impaired water bodies, they may drain into streams, lakes, and estuaries. Wetlands are unique environments for mercury cycling. With the large surface area, shallow water depths and substantial emerging vegetation, wetlands act as efficient traps of the large amounts of atmospheric deposition that they receive. Methylation rates in wetlands are also higher than in other water bodies (Hurley et al 1995) due to low hydraulic gradient (resulting in longer contact time), high organic matter content, active microbial community, and favorable sulfate/sulfide concentrations. Wetlands are recognized as important sources of methylmercury for freshwaters. The food web structure in wetlands also can be expected to be substantially different than in streams and lakes and is likely periphyton-based. If there are abundant wetlands in an affected watershed, sampling should be conducted for important parameters such as total and methylmercury in wetlands and in waters draining them, mercury and methylmercury concentrations in sediments, and overall methylation efficiency and export rates.

<u>Streams and Rivers</u>: Streams and rivers may require a different approach to sampling than lakes or wetlands. "Impaired" segments may be lengthy which can result in a high degree of spatial variability. This is particularly true when tributaries constitute a major portion of the area and mercury load. Changes in runoff in different times of the year can also significantly change the mercury and methylmercury load associated with suspended sediments. Hence, it is important to capture the seasonal variations by collecting an adequate number of samples during different times of the year. Depending on the gradient and depth of the stream, the primary producers can be either periphyton

or phytoplankton and may vary from one portion of the river to the other. Large amounts of contaminated sediment also may be transported from urban areas, mine sites, or other contaminated areas (in particular creeks), and sampling intensity should be adequate to capture this spatial variability.

Estuaries: Estuaries are meeting points of freshwater streams and seawater, and salinity within the estuary can be different depending on the location within the estuary. Since seawater typically is lower in mercury concentration and coagulation and precipitation reactions may remove some of the mercury delivered from the streams and rivers, lateral variations in mercury concentrations can be high within an estuary. Additional sulfate derived from sea salt may be reduced in anoxic environments, causing significant changes in mercury speciation and bioavailability. Increased chloride concentrations in seawater also can change mercury and methylmercury speciation and affect bioavailability. Generally, methylation is lower in estuarine water than in freshwater resulting in substantial differences in BAF values in estuarine vs. freshwater fish. Because the fish types as well as the methylation rates and fish tissue concentrations are very different between estuarine and freshwater systems (Gilmour and Riedel, 2000). BAFs developed for freshwater systems should not be used for estuarine portions of the river. Seasonal variations also can be considerable within an estuary, and changes in mercury and methylmercury concentrations may arise as a result of changes in freshwater flow, lunar cycle, etc. In addition to measuring total and methylmercury, concentrations of sulfate, sulfide, chloride, redox, DOC, pH and other parameters also should be quantified.

## 4.3.1.3.3 Analytical costs for mercury and methylmercury

Sampling and analysis of mercury and methylmercury in environmental samples can be very expensive due to the clean protocols and strict QA/QC standards. An attempt is made here to provide the reader with an idea as to the approximate costs involved in analyzing samples for mercury and methylmercury. Please note that the estimate provided here is meant as a reference point and the actual price may vary substantially between laboratories (most of the quotes below are approximate values obtained from certified laboratories). The costs involved in sampling (labor, materials and supplies etc), shipping, and additional costs for QA/QC samples (e.g., field blanks, duplicates) are *not* included in this estimate as the total number of samples required for each water body will be variable.

Water Samples Unfiltered Total Mercury Filtered Total Mercury Unfiltered Methylmercury Filtered Methylmercury pH, Temperature, Redox Sulfate Sulfide DOC	\$85 \$120 \$190 \$230 \$30 \$15 \$20 \$35
<u>Fish Samples</u> Total Mercury (including sample homogenization) Fish Gut Content – Trophic Level 3	\$155 \$150

Fish Gut Content – Trophic Level 4	\$150
Sediment Samples	
Total Mercury	\$200
Methylmercury	\$220
Benthic Community Structure	\$200

Based on the above estimates, the total cost of sample analysis at one sampling location is estimated at \$1,800. To put this in perspective, the total cost for laboratory analysis of these parameters for sampling at 10 locations in a water body, three times a year, would be approximately \$54,000.

#### 4.3.1.4 Improvements in Load Modeling

As previously mentioned, both the WCS and WASP5 model used to estimate mercury loads from the watershed include a number of empirical parameters, and the choice of values for these parameters can significantly alter estimated loads (and therefore load assignments to point sources). While it may not be practical to estimate every single input parameter value for each watershed, improvements can and should be made to some key parameters in the model by choosing input values that are more representative of the watershed conditions rather than using a single value for all watersheds.

The choice of appropriate wet and dry deposition rates for mercury in a watershed is critical. If monitoring stations are available within a watershed where the TMDL is being developed, those data should be used (averaging multiyear data) in lieu of national data. If local data is unavailable, careful review of RELMAP results and MDN data should be conducted to see which of those two might better represent the depositional rates within the watershed.

In the WCS model, soil-water partitioning of mercury ( $K_d$ ) can vary over several orders of magnitude for various soils. Instead of using a single value for all types of soil, it would be better to use soil-specific  $K_d$  values (extrapolated from literature based on TOC, grain size, etc.). Current modeling efforts have assumed that mercury loads from the watershed are primarily a function of atmospheric deposition, but data seem to indicate that soil organic matter plays an important role in determining mercury retained in soil (Adriano, 1986 and AMEC, 2002, unpublished data). This result needs to be accounted for in the models.

As described earlier, simulated mercury export rates from watersheds are inversely related to the mixing depth ( $z_d$ , depth to which atmospheric mercury is incorporated in the soil profile). Contrary to EPA's assumption of atmospheric mercury building up in the top 2 cm of the soil, recent evidence suggests that mercury concentrations are nearly uniform at least in the top 15-20 cm of the soil. EPA's assumptions with regard to the mercury balance in surface soils apparently are based on Lindberg's work at Oak Ridge National Laboratory, as cited in Mercury Study Report to Congress. However, this assumption needs to be carefully evaluated in light of recent data. We strongly recommend that soil profiles be collected and analyzed in watersheds as part of TMDL sampling, and mercury concentrations be measured to determine the mixing depth for mercury in the soil. Such studies also can yield important information on the amount of

"background" mercury ( $C_0$ ) that is in the soil. Since the selection of these parameters ( $C_0$  and  $z_d$ ) has important implications for the source (and the load) of mercury in the water bodies, we note that it should be based on a thorough review of existing data for soil concentrations, preferably site-specific measurements, and not founded on untested speculation.

The WASP5 model used to determine the fate and transport of mercury also is affected by the choice of various reaction rates and constants. These rates differ widely between aquatic systems. The selection of parameters should be based on a critical review of literature, and sensitivity analyses should be carried out on model runs to identify most sensitive parameters. Load estimates from point sources should take into account mercury present in intake water so that the "background" mercury is not double accounted in point source loads and in nonpoint source loads.

#### 4.3.1.5 Phased TMDLs

Phased TMDLs are an approach that may be used when time constraints (like courtordered schedules) prevent EPA and the states from collecting and analyzing all of the information highlighted above as necessary to make informed load reduction and allocation decisions. The phased approach is an iterative process that provides for pollutant reduction, to the extent that any can be justified on the basis of existing data, while additional data are collected and the efficacy of existing controls are evaluated. Such TMDLs require a monitoring plan to verify reductions and assessment of progress toward achieving standards. If standards are not achieved after a specified period, data obtained through the monitoring effort may be used to revise the TMDL. Phased TMDLs are advised in particular where data, models, and predictive tools are not well developed; a situation ideally suited to mercury (US EPA 1995).

Phased TMDLs are appropriate in at least two instances: 1) where there is some confidence that the standard can be attained through the control of nonpoint sources and monitoring data collected during the first phase is used to verify progress toward attainment; or 2) where there are large uncertainties and the phased TMDL takes steps towards attainment, reducing the uncertainties in subsequent phases. The use of phased TMDLs fits well with the concept of identifying and quantitatively reducing uncertainties as discussed above.

The Agency's use of phased TMDLs in the case of mercury is reasonable and appropriate with respect to expected load reductions from nonpoint sources. The use of the time to assess the reductions of atmospheric deposition brought about by the Maximum Available Control Technology (MACT) implementation is especially relevant and beneficial. Reasonable assurance in this case is provided by statute. Monitoring of affected water bodies is essential during this time period to assess the efficacy of implemented air controls. As noted earlier, load reduction burdens on point sources are premature in these TMDLs.

There are two concerns regarding the use of phased TMDLs by the states in the case of mercury.

First, proper baseline measurements are not in place at this time to measure against future conditions, and resources are not available to competently assess the efficacy of various MACT implementation. We do not know enough at this time about how mercury

concentrations vary seasonally and year-to-year to make intelligent decisions about fish and water quality trends over a relatively short time period (e.g., five years). Perhaps comprehensive and well-funded monitoring programs will generate adequate data to get the kind of answers that are required, but such programs will need to continue for substantial periods of time (> 20 years) in many cases.

Second, there are huge uncertainties associated with the interpretation of narrative standards for water bodies within states or regions due to the difficulties associated with translation of fish tissue-based criteria to water column-based criteria. The development of water column-based standards should not be a goal of phased TMDLs as they are unnecessary and inappropriate at this stage. Trends in fish and water quality data and, thus, the efficacy of air emission controls being pursued by the Agency under MACT can be assessed without the development of water column-based quality standards. Data collected during phased TMDLs can be used to better understand the nature of the ecosystem under study (e.g. methylation and bioaccumulation) and ultimately may be used as part of an adaptive management strategy if air emission controls fail to achieve the required results.

#### 4.3.1.6 Time Required to Attain Criteria

Time to attain criteria is difficult to predict. It may become clear as time and science progress that there are situations where attainment simply is not possible. In these cases, states may elect to develop a site-specific criterion reflecting the actual concentration, and/or to perform a Use Attainability Analyses (UAA) for certain of these waters. There appears to be no guidance currently available for states to address this issue.

There are some simple models for predicting rate changes in fish tissue levels but the reliability of those models is questionable given the complexity of mercury biogeochemistry. Equation (4-4) (reproduced below) provides a link to the methylmercury load and calculates organism body burden as a function of uptake and depuration rates. As previously discussed, this equation is intended to provide estimates of body burden for a trophic level 1 organism; however, linked systems of equations can be written and solved to model the body burden of higher level organisms. Alternatively, the uptake rate can be viewed as a lumped parameter representing the aggregate uptake rate for an organism at any trophic level within the system. Viewing the equation in this way, several observations can be made.

$$C_0 = \frac{L}{k_2 M_0} \left(1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2}\right)$$
(4-7a)

At steady state, the body burden of the organism is given by the quantity  $L/k_2M_o$ . At first, it may seem unlikely that the final body burden is controlled by the methylmercury production rate and the depuration rate and has nothing to do with the uptake rate. However, on further inspection, it makes sense because, in this model the only removal mechanism for methylmercury from water is biological uptake. Eventually all the methylmercury production goes into the organism or builds up in the water column. Therefore, the uptake rate constant simply meters how quickly the transfer takes place

from the water to the organism, but does not affect the final partitioning of mercury between the organism and the water.

By substituting some realistic values for the quantities  $C_o$ , L, and  $M_o$ , the rate constant  $k_2$  can be estimated. If we assume that  $C_o$  is approximately 0.5 mg/kg at steady state (averaged over all fish species in the water body), an estimate of methylmercury production rate is 0.5 g to 5 g / km<sup>2</sup> - yr (Ullrich et al 2001). An estimate of the standing fish biomass for an oxbow of the Savannah River is 121 kg/ha or 0.012 kg/m<sup>2</sup> (Schmidt and Hornsby 1985). Adjusting units (so that the methylmercury production rate is in mg /m<sup>2</sup>-day (we used a mid-range value of 2 g / km<sup>2</sup> - yr or 5 x 10<sup>-6</sup> g / m<sup>2</sup> - day), substituting into the equation

$$C_0 = \frac{L}{k_2 M_0}$$
 (4-7b)

and solving for  $k_2$  gives a value for the depuration rate of approximately 0.00083 /day.

Using this constant and assuming simple first order depuration of methylmercury from the fish gives concentrations of 0.73 of the initial fish tissue concentration after one year and 0.22 after five years. This is probably an overestimate of the rate at which methylmercury is depurated fish tissue, not necessarily because the rate constant is inappropriate, but because even as loads diminish to the aquatic system, the fish continue to accumulate mercury. Ideally, the differential equation that models the organism concentration could be solved assuming an initial concentration in the organism other than zero. Then beginning with an initial concentration reflecting the impaired condition, the methylmercury loading (production) rate could be adjusted downward to emulate the reduction of loads and the time to attain a target value in fish tissue could be determined. Of course, the use of local estimates of L, C<sub>o</sub>, and M<sub>o</sub> would give a more accurate estimate of the depuration rate for a biological system in a given water body. The same caveats apply to this calculation as to the calculation of BAF from fish tissue data where there is uncertainty of the condition of the food web vis-à-vis steady-state conditions.

# 4.3.1.7 Use of current criteria as interim standards

#### 4.3.1.7.1 Existing water column criteria

A number of states have adopted the 12 ng/L standard for mercury. These same states more than likely have a narrative statement that could be interpreted numerically for the protection of human health. An important question then is, would the 12 ng/L value be protective if adopted?

In the TMDL document for the Savannah River, EPA stated that the 12 ng/L standard was not protective because there obviously were fish that exceeded the State of Georgia fish consumption guidelines, indicating a restricted use of the water body for fishing, and also exceeded the FDA action level of 1 ppm. In comments to EPA, it was pointed out that exceedance by a fish, fish composite, or even a fish species did not automatically imply impairment of the water body, because the risk to consumers is based on a variety of fish consumed from various trophic levels. EPA acknowledges and has used this

approach in the development of its methylmercury criterion. Furthermore, in its October 2000 guidance for the use of fish and shellfish advisories for § 303(d) listing decisions, EPA acknowledges that "in some cases, fish and shellfish consumption advisories may not demonstrate that a section 101(a) "fishable" use is not being attained in an individual watershed." Nonetheless, in the same document, EPA admonishes the states to "translate the applicable narrative criteria on a site-specific basis."

Multiple criteria are not needed and should not be adopted to achieve the same goals. For instance, if a fish tissue-based criterion is adopted and a water column-based criterion is also in place, conflicts inevitably will arise. In such cases, there would be confusion as to which criterion would be used to determine exceedance of water quality standards and which would control listings. Further confusion with regard to mercury standards is undesirable. States with multiple human health criteria would need to clearly prioritize those situations in which certain criteria would govern, or develop rules for situations in which conflicts between criteria might arise.

However, if a state opted to rely on its 12 ng/L criterion as its sole basis of regulation, we offer the following observations concerning the degree of protectiveness for human health of this value. First, as has been previously mentioned, the 12 ng/L criterion was developed by dividing the 1 ppm FDA action level by a BCF measured in laboratory studies for freshwater fish species. These studies showed that brook trout exposed to 30 ng/L of methylmercury contained 1 mg/kg in muscle tissue and that fathead minnows exposed to 18 ng/L of methylmercury contained 1.47 mg/kg with a resulting BCF of 81,700. While the bioconcentration factor established in this latter study was termed a BCF, in the text, the authors acknowledge that the higher BCF values found in this study versus others might have been due in fact to bioaccumulation resulting from grazing of the minnows on <u>Aufwuchs</u> growing in the test solution. We note that these methylmercury concentrations are quite high when compared to methylmercury levels seen in natural systems.

Second, while the authors of the 1984 mercury criteria document offer that the 12 ng/L is a standard which assumes that all discharged mercury is methylmercury, they eventually recommended that the value be adopted in terms of total recoverable mercury, with the caveat that the standard might be overly protective when based on the total recoverable method.

Assuming that the 12 ng/L is adopted for total mercury and we use a reasonable percentage of this mercury as methylmercury (say 5%), then the resulting standard in terms of methylmercury is 0.6 ng/L. Furthermore, if the BCF of 81,700 is applied to this methylmercury level, the corresponding fish tissue would be 0.05 mg/kg, a concentration that by most standards would be acceptable. If we assume that the BCF is truly that, rather than a BAF, and augment it with a food chain multiplier of 5 – 6 per the Mercury Study Report to Congress, the resulting BAF would be of the order of 490,000 and the resulting fish tissue concentration would be 0.29, a number very close to EPA's criterion. If, however, a methylmercury percentage higher than 5% and BAFs greater than 500,000 L/kg were to be assumed, then the use of 12 ng/L probably would be less protective although within a range states may find acceptable. In addition, the effects of environmental factors such as pH, DOC, temperature, redox, and other factors that may have an impact on bioaccumulation are not taken into account in the laboratory studies in which the 12 ng/L standard was derived.

## 4.3.1.7.2 Other Criteria – Great Lakes

The Great Lakes water quality guidance embraces four criteria -1.8 ng/L (total) for the protection of human health, 1440 ng/L (dissolved) for acute aquatic effects, 770 ng/L (dissolved) for chronic aquatic effects, and 1.3 ng/L (total) for protection of wildlife. The criteria for the protection of human health and wildlife already have received significant comment. Suffice it to say that the methodologies by which they were derived is still a subject of controversy. We would judge the application of these criteria during a phased TMDL to be overly protective.

4.3.2 Load Reduction, Allocation and Permit Limit Derivation - Review of Current Regulatory Approaches

Load reduction, allocation and the development of permit limits are premature in the first phase of a phased TMDL for mercury. However, this topic is of great importance and EPA should provide guidance to the states on how it should be done in subsequent TMDL phases. In this section, we will review and offer constructive feedback on the load allocation strategies that have been pursued in certain TMDLs already completed by EPA. We are aware of several, including the Savannah River TMDL, the EPA Region 6 Louisiana TMDLs, and the Florida Everglades TMDL.

#### 4.3.2.1 Load Reduction and Allocation Strategies

#### 4.3.2.1.1 Savannah River TMDL

Approach: The Savannah River TMDL was based on the assumption that atmospheric deposition accounted for 99% of the mercury load to the river and less than the remaining 1% came from point sources. The TMDL developed an estimate of the non-point source loading to the River and its tributaries of approximately 58 kg/yr out of an estimated 186 kg/yr of atmospherically deposited mercury. This represents an annual transport from the watershed into the water body of about 32% of the deposited mercury.

The overall load reduction strategy was tied to simulated concentrations in the river. Model simulations using the watershed loading model linked to an aquatic fate model were used to simulate a concentration profile for the river. The highest modeled concentration in an individual segment was then compared to the water quality target of 2.8 ng/L, developed from locally measured BAFs and methylation translator. This comparison (1 minus the ratio of the water quality target to the highest modeled concentration in a segment) was the specified load reduction.

Comment: The assumption that 99% of the load to the river is derived from recently atmospherically deposited mercury (as opposed to other nonpoint sources) was never justified by EPA or supported by data, although such justification and support was requested on a number of occasions in comments to these TMDLs. It is entirely possible in these watersheds that much of the mercury comes from older anthropogenic or natural background sources. The estimate of 32% of the annually deposited mercury

being transported from the watershed to the water body seems very high given what we know about the transport of other heavy metals in soils to aquatic systems. Recently, for instance, Krabbenhoft et al (1995) calculated an export rate of only 4% for the Allequash Creek Watershed, a relatively small (21.8 km<sup>2</sup>) watershed in northern Wisconsin. EPA Region 4 modelers claimed that this percent transport from the watershed was necessary to yield a load to support the concentrations of mercury in the river. However, the WCS model used to estimate the loads did not consider any terrestrial component of pre-industrially deposited mercury, weathering of natural materials, or any other inputs to the aquatic system such as shallow groundwater. Studies are currently underway by EPRI to better quantify the contribution of terrestrial mercury. By not accounting for this component of mercury loading in watersheds where fluvial processes such as runoff and erosion dominate loadings to water bodies, TMDLs will contain uncertainties regarding the contribution of atmospheric deposition of mercury, the effects of that loading on fish tissue levels, and the efficacy of air emission controls on restoring beneficial uses. However, it is reasonable and fitting in light of the direction EPA appears to be taking in its pending TMDL guidance that an adaptive management strategy, focusing first on the implementation of existing air regulations, be pursued in upcoming mercury TMDLs.

In order to calculate the load reduction from nonpoint sources required to achieve the TMDL, EPA utilized the following formula:

$$TMDL \ Load = \frac{(WQT) \ (Current \ Average \ Annual \ Load)}{(Highest \ Modeled \ Segment \ Concentration)}$$
(4-8)

We believe this approach is inappropriate for several reasons. First, EPA used the highest predicted value from the modeled segments. Figure 10 in the Savannah River TMDL document shows that the model overpredicts total mercury concentrations in this segment under low flow conditions on the order of 30%. A comparison of Figures 10 and 12 in the TMDL document show that the predicted total mercury concentrations in this segment drop by almost 1 ng/L (about 15%) under average flow predictions. Yet, Figure 12 shows that the predicted concentrations under average flow conditions are still higher than the observed concentrations under low flow conditions. We can only conclude that the simulated average flow concentrations are too high, which lead to an overly conservative estimate of the amount that loads need to be reduced. We would suggest that a more reasonable estimate of the concentration in this segment under average flow conditions could be made by reducing the observed concentration in the segment by the ratio of the predicted concentrations under average and low flow conditions. This would result in a concentration of approximately 85% of the observed low flow concentration or about 3.8 ng/L. The resulting TMDL load would then be 43.8 kg/yr rather than 32.8, which suggests a load reduction of 15 kg/yr rather than 26 kg/yr, or 25% rather than 44% of the input load to the watershed, to meet the TMDL.

The second reason we take exception to EPA Region 4's approach is that the designation of segments in the model is based on physical properties of the stream channel that have no correspondence to the segments of the river listed by the State of Georgia under § 303(d). We agree that the listed segment from Ebenezer Creek to the Tide Gate likely has the highest water column mercury and fish tissue concentrations along the main stem of the river and that this segment corresponds roughly to model segments 29, 30 and 31. Thus, we contend that a more reasonable value to use in the

TMDL load calculation is the average concentration in these three segments under average flow conditions. If we apply the same logic as above but use the average concentration in these three segments, rather than the highest, we calculate a concentration of about 3.4 ng/L. Thus, the TMDL would be 48.9 kg/yr, a required reduction of 9.8 kg/yr, about 17% of the input load.

If fish truly "move throughout the watershed" as EPA claims on page 19 of the TMDL document, then EPA should not have based the load reduction on any one segment at all, since fish would be exposed to the full range of concentrations occurring in the river. Rather, it should calculate load reductions based on the difference between the average concentration in the river and the WQT. In this case, the geometric mean of the data observations of total water column mercury is 2.41 ng/L. As the WQT is 2.83, the average concentration in the river and tributaries is below the WQT and no load reductions are required. EPA easily could have calculated the average simulated concentrations from its average flow scenario and computed the required load reduction in a like manner.

#### An Alternative Perspective on Load Reduction Calculation

EPA calculated in the Savannah River TMDL document that the current mercury load to the Savannah River is 58.77 kg/yr. It then calculated a TMDL of 32.78 kg/yr based on an average flow and a WQT of 2.83 ng/L. EPA went on to state that the difference in these two numbers is the required load reduction. We disagree with this notion. We contend that the bioaccumulation in fish is not driven by the input load to the system, but rather that portion of the input load that is retained in the system.

Using data presented in the TMDL document, one may calculate the load that leaves (flows out of) the Savannah River on an annual basis. If we use 5 ng/L as the total mercury water column concentration (Figure 12 in the Savannah River TMDL document) and multiply by the flow rate at the end of the most downstream segment (350 cms), the annual mercury load exiting the river is 55.2 kg/yr. The difference between the input and output loads, therefore, is about 3.5 kg/yr. We contend that this load, the net retention of mercury in the river, is of much greater importance than the input load. It is this retained load, rather than the input load, that is available to be bioaccumulated by fish. Thus, it could be argued that the required load reduction is 3.5 kg/yr rather than the 26 kg/yr proposed by EPA. While not generally required or needed as part of a TMDL, watershed mass balance considerations should be an important part of mercury TMDLs, where diverse sources of loadings to the water body, export from the water body (including evasion) need to be accounted for.

A corollary of this argument is that the concentration of total mercury in water is not a very effective tool to manage bioaccumulation of mercury in fish. If the accumulation of mercury in fish were an equilibrium, rather than a time-dependent phenomenon, the input load and the resulting concentration in water would be more relevant. However, since fish bioaccumulate mercury over a long period of time, the mercury available for methylation in sediments is much more relevant than the water column concentration. It may be that the retained mercury load, rather than the input load, is more important in explaining the uptake of mercury into fish.

4.3.2.1.2 EPA Region 6 - Louisiana TMDLs

EPA Region 6 has developed TMDLs for mercury in six water bodies in Louisiana. The Region 6 approach involved the calculation of a reduction factor (RF) by dividing a fish tissue concentration (MC) in the worst case species by a "safe tissue concentration" (SC), a risk-based value which included a margin of safety. Region 6 used a value of 0.4 ppm as the safe concentration, which was derived by starting with a value of 0.5 ppm and applying a margin of safety of 20%. The worst-case species fish tissue concentration was taken as the average bowfin concentration in Bayou Plaquemine Brule of 1.191 ppm.

The next step in the Region 6 procedure was to calculate the TMDL by dividing the total atmospheric deposition (EL) by the RF. The total atmospheric deposition was taken as the mean wet deposition of three Mercury Deposition Network stations plus 25% of the wet value to account for dry deposition. The resulting load was 345.5 ng/m<sup>2</sup>-day or 18  $\mu$ g/m<sup>2</sup>-yr.

The technical concern with this analysis and approach is that it is unlikely that such a 1:1 relationship exists between atmospheric deposition and water column or fish tissue concentrations, except in special situations (e.g., the Everglades or a seepage lake where the surface area of the water body is large compared to the watershed). The Florida TMDL pilot study demonstrates that, even though the model is linear and the modeled system is assumed to be linear, the response of the system to reductions in atmospheric deposition is not linear, most notably for large reductions of atmospheric load. Presumably, this is because there is some mercury in the system not directly of atmospheric origin. When atmospheric inputs become small, then watershed sources of mercury begin to dominate the amount of mercury in the water column and ultimately the response of the fish.

These systems can be viewed in terms of an electrical analogy where the atmospheric deposition is the input signal, the watershed/river system is a capacitor and the mercury in fish tissue the output signal. If the capacitance (watershed) is small or zero, then the input signal and output signal should be of similar magnitude (i.e., have a 1:1 relationship). If however, the capacitor (watershed) is large, then the discharge from the capacitor dominates the output signal and masks the input signal. In a system like the Savannah River, we must assume the capacitor is large, because the watershed is huge compared to the water body. In fact, assuming that soils in the basin have a typical mercury concentration of 100  $\mu$ g/kg, the top ten centimeters of soil alone contains from 500 to 1000 times the annual atmospheric deposition. In such systems, the reduction in the input signal does not lead to similar reductions in the output, or may take a very long time to be observed.

#### 4.3.2.1.3 Florida Everglades TMDL Study

The Florida Pilot Mercury TMDL Study was prepared for the Florida Department of Environmental Protection (DEP) and funded by EPA. It focused on a very different reduction and allocation issue — the apportionment of air deposition into local, regional, and global sources. It was an attempt to integrate EPA's best air and mercury cycling models and science to develop a mercury TMDL for the Florida Everglades and a protocol by which other such TMDLs can be developed. By its own admission, the study fails to do this. The opening paragraph of the document states: "Because this is a pilot study with essential information missing or incomplete, it is not being developed by Florida with the expectation of implementing changes in source permits or other action. It provides the technical analysis for a more comprehensive discussion of the full TMDL process to be created subsequently."

It is of interest to note that of the eight essential elements of a TMDL outlined on pages 5 and 6, this pilot project, according to the report, was unable to complete seven of those eight elements. Interestingly, the only one that can be completed was the public participation element.

Approach: The modeling exercise relies on characterization of representative clusters of atmospheric conditions in South Florida and emissions rates developed by EPA for various mercury emission sources to model mercury deposition. Data from the Florida Atmospheric Mercury Study (FAMS), alluded to in this report, is summarized in the literature, but our understanding is that the data itself has not actually been published. The air modeling study uses emissions from EPA's Mercury Study Report to Congress (1997). Using these emissions rates for local sources, the deposition model was then "calibrated" to achieve the bulk deposition rates observed in South Florida. While the measured bulk deposition rates include the effects of global, regional, and local sources, the model calibration essentially forced all the deposition to be accounted for by local sources (the so-called Base Case scenario). A second scenario was run that uses actual stack testing data for the two major local sources. When this was done, the modeled deposition estimates drop to 57% of the base case. A third scenario was developed in which actual stack testing data for all local sources was utilized. In this case, the deposition estimates drop to 36% of the Base Case. Thus the actual local atmospheric emissions would appear to require a reduction of only some 34% to reach the target, while EPA claims that a reduction of 76% is required.

Comment: In this pilot study, in our opinion, EPA artificially inflated the impact of the local sources and then suggested that large reductions were required in order to achieve the desired reductions in fish tissue. EPA assumes that any uncontrollable background air sources which contribute to the water quality impairment will have to be "made up" by point air emission sources. Furthermore, because of EPA's stated conclusion in this report that

"Until measurements or models allow us to constrain the uncertainties in the long-distance transport phenomenon there is no objective basis for addressing this question",

it appears that local emission sources may be called upon first to bear the impact of required atmospheric load reductions. Under the presumption of this document, local sources will have to reduce by more than their fair share to achieve the load reductions required from the uncontrollable global and regional sources. As voiced by EPA in the document

"When reasonable lower limits of global loadings are considered, our results indicate that virtually complete elimination of local sources is likely required to approach or achieve reductions in mercury concentrations in largemouth bass consistent with achieving the target level of 0.5 mg/kg."

Using this logic, it may be counterproductive for a local source to demonstrate that emissions beyond their control are the cause of the problem, as EPA simply may require even greater reductions from the local source to account for the uncontrollable background sources. This approach to load allocation places an unfair and undue burden on domestic industry. Sources should be asked to do no more than to contribute their fair share of emissions reductions.

## 4.3.2.2 Mercury Source Identification

Identifying the sources of mercury between and among point and nonpoint sources is a very difficult task to accomplish. In some cases, such as a seepage lake or other water body which has relatively little contribution to the mercury load from watershed runoff or erosion and where the main source of mercury is atmospheric deposition and well defined point sources, it may be possible. However, in systems with large watersheds where the mercury in the water body is a function of the washoff and erosion of atmospherically derived mercury retained in the watershed, such specific source identification is virtually impossible at this time. The reason is that there is an enormous pool of mercury in watershed soils. This mercury has been derived from a variety of sources over a period of many years, many of which predate the industrial era. Mercurv associated with recent atmospheric deposition, older industrial deposition (which cannot be controlled by implementation of emission controls to existing air sources), other natural sources from outside the watershed (volcanoes, forest fires), and naturally occurring mercury within the watershed (released by the weathering of native rocks and soil materials) cannot be distinguished. Until the science and data advance, we cannot make reliable distinctions between existing atmospheric sources, point sources, and all other sources. Data collection during phased TMDLs could be oriented toward this goal. Except in those limited situations in which point sources can be shown to be causing excursions of numeric water quality criteria, load reduction burdens on such sources are inappropriate.

There are several studies underway which may make some advances in our ability to identify and quantify mercury sources. The METAALICUS study currently being funded by EPRI and other organizations involves the use of stable isotopes of mercury being deposited in a Canadian watershed. Tracking of this "tagged" compound hopefully will yield some data to help resolve this issue. Another study being funded through EPRI in South Georgia hopes to use analogies between plutonium, a recently anthropogenically deposited radioisotope, and mercury to estimate washoff and erosion rates of recently deposited mercury in a watershed where fluvial processes dominate the loading of mercury to the water body. Yet another promising recently published study (Jackson 2001) uses variations in isotope composition of mercury in a freshwater sediment sequence and food web in an attempt to differentiate older from more recently deposited mercury.

Several pieces of evidence point to the inherent difficulties in identifying and quantifying sources. For example, in the case of the Savannah River and the South Georgia rivers, the Savannah, which has at least two major point sources, has lower levels in fish than the South Georgia rivers, which ostensibly have no major point sources. There also is evidence (presented earlier in this document) within the Savannah itself that the highest levels of methylation, and correspondingly highest levels of mercury in fish, occur in the tributaries and not in the mainstem (the mainstem was where the § 303(d) listings

occurred). This is powerful evidence suggesting that the point source discharges to the mainstem were having little effect on mercury levels in fish and human health risk. The lack of a direct linkage between the discharger and the impairment begs the question of whether there is a justification, within the bounds of the legal interpretations of the Clean Water Act, to regulate such a discharger. The complexities of mercury biogeochemical processes may preclude establishing such direct linkages in many cases.

Data collected by Dr. Randall Manning of the Georgia Environmental Protection Division demonstrates another important point concerning mercury; that is, methylation rate is probably a more important factor than loading rate in determining fish tissue concentrations. His data show that the geographic location of a river basin in the state is a major determinant of mercury concentration in fish – south Georgia rivers tend to have 4 to 5 times higher concentration than north Georgia and Piedmont rivers, despite the fact that there are more anthropogenic mercury sources in the northern part than in the southern part of the state. This conclusion also is supported by the data of Couch (1997), who concluded that biological tissue concentrations are higher in the Coastal Plain of Georgia, even though mercury sediment concentrations are higher in north Georgia and the Piedmont. This conclusion is supported further by analysis of fish tissue concentrations within the Savannah River, which shows higher concentrations as one moves for the northernmost reaches of the river in the Piedmont, to the southern reaches of the river in the Coastal Plain. Such data argues against direct links between dischargers or emitters of divalent mercury and methylmercury in fish. If such direct links cannot be established (or at least quantified vis-à-vis the background watershed loads), it is difficult to imagine how meaningful allocations can be made.

# 4.3.2.3 Permitting Strategies

In terms of the development of permit limits, EPA Region 4 has taken a position in its Savannah River and South Georgia TMDLs. EPA Region 4's approach for the Savannah River is reviewed and commented on below.

Approach: The assumption that 99% of the mercury loadings to the Savannah River was of recent atmospheric origin played a large role in the permitting strategy. The implication obviously is that 1% or less of the mercury load comes from point sources and other nonpoint sources. This logic led Region 4 to advance the concept that point sources were *de minimis* contributors to the mercury problem. Notwithstanding their presumed minimal contribution, EPA concluded that load reductions from point sources would be required. It proposed an alternative (left up to state regulators) of giving dischargers an end-of-pipe criterion equal to the water quality target or of monitoring and developing, as necessary, minimization plans. A facet of EPA Region 4's approach was to give a credit for mercury originating from a facility's intake water. However, there is uncertainty whether EPA intended this to be a concentration or mass credit. EPA Region 4's implementation plan did not include language relevant to mixing zones, although criteria, if adopted as permit conditions, were assumed to be at end-of-pipe. EPA Region 4 did not address water conservation measures and its impact on effluent concentrations, although this is becoming more and more an issue as population levels and water demands increase.

Comment: EPA did not establish an adequate basis for allocating load reductions or assigning permit limits to point source dischargers in this TMDL. EPA stated on page 50

of the TMDL document "that approximately 99% of mercury loadings to the watershed is from atmospheric deposition" and that "a 44% reduction of mercury deposition is needed to achieve the TMDL." EPA expects these reductions to be achieved through full implementation of current Clean Air Act (CAA) MACT programs by 2007. EPA further stated that "approximately 1% of the current loadings of mercury to the River is from NPDES point sources," having "no discernable impact on water quality in its present condition." These discharges "would not cause the water to be impaired should the water be restored to full health" and that "elimination of such discharges through extremely stringent effluent limitations, may be very expensive if not technically unachievable." EPA concluded in the TMDL document that "such elimination or stringent reductions of mercury are not necessary to meet the TMDL since reasonable assurance is provided that air sources of mercury will achieve their load allocation." Given its position, EPA should have allowed point sources to continue discharging at their current levels, rather than requiring Georgia to select between a "criteria end of pipe" effluent limit or a mercury minimization program.

"Current levels" should not be translated into an existing effluent quality limit in a permit. Reliably quantifying existing mercury levels in a discharge, including the existing variability in those levels, both in the short- and long-term, would require extensive longterm data collection and analysis using Method 1631. Instead, current levels can be maintained without the need for NPDES permit changes. Permittees would be expected to comply with the conditions in their permit requiring notification of certain plant modifications. That notification process would alert regulatory authorities to possible changes in the status quo that might warrant additional regulatory consideration. This should be the case any time a discharger is determined to be *de minimis*.

#### 4.3.2.4 Mixing Zone Restriction

These comments are made in consideration of language in EPA's Final Rule to Amend the Final Water Quality Guidance for the Great Lakes System to Prohibit Mixing Zones for Bioaccumulative Chemicals of Concern.

EPA asserts that the use of mixing zones can only increase the allowable discharge of PBTs to water bodies. We do not agree that allowing a discharge above the water quality criterion in a small portion of the water body will lead to an exceedance of the methylmercury criterion in fish. Mixing zones were originally designed to allow toxicity above acute and chronic levels to occur in water bodies and were designed to protect against toxic effects to fish based on concentration. Bioaccumulation of mercury in larger fish, especially piscivorous fish with large home ranges, would likely be minimally affected by localized water column concentrations in the vicinity of an outfall. We believe the effects of these chemicals are in fact mitigated by dilution, contrary to EPA's assertions in the Federal Register. If not, how could lowering water column concentrations by reducing pollutant loadings reduce levels in fish? This is the underpinning of the entire TMDL approach for mercury, not to mention the use of BAFs.

EPA also suggests that mercury mass, as well as concentration, poses an environmental problem. However, it has been documented that mass loading of mercury into a water body has little to do with tissue levels in fish (see previous comments in this document). Both of these lines of evidence raise valid concerns for the need to regulate point sources by eliminating mixing zones and holding point sources accountable for meeting water column criteria for mercury. While EPA may believe that it is good policy to minimize overall loadings of mercury in the environment, there is little evidence to support the notion that reduction of inorganic mercury from point sources in a particular water body will result in a localized environmental benefit.

Mercury in most wastewater discharges is not in the methyl form and, therefore, might not be considered as a "bioaccumulative" toxicant. Only when methylated in the watershed does it become a problem. There are numerous studies showing that the bioaccumulation of methylmercury in fish is associated only weakly with loading rates of inorganic mercury.

In the water quality guidance for the Great Lakes System (40 CFR 132), Appendix F (Procedure 3.E.3) procedures allow for the use of mixing zones for pollutants that degrade where scientifically valid studies demonstrate that degradation (including chemical speciation, and biological and chemical transformation) is expected to occur under the full range of environmental conditions. Reduction of mercury to the elemental form (Hg<sup>0</sup>) and subsequent volatilization (evasion) to the atmosphere constitutes such a biological transformation and results in a net loss of mercury from the water body.<sup>16</sup> In water bodies where evasion is a significant factor, mixing zones would be appropriate to translate acceptable water column levels to end-of-pipe concentrations.

As previously mentioned, mixing zones seem to be appropriate when the implementation of water conservation measures cause a rise in mercury concentration across facilities, but where the overall mass of mercury is being lowered. In such cases, mixing zones should be allowed to bring the concentrations back to acceptable levels in stream, thereby providing an incentive for discharges to reduce water use.

<sup>&</sup>lt;sup>16</sup> See Chapter 11. Supporting documents. Final water quality guidance for the Great Lakes system: Supplemental information document (NTIS # PB-95187266).

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## Appendix A. Description of the Reference Dose Derivation

A.1 What is a Reference Dose?

Risks from health endpoints other than cancer are limited by the use of an exposure limit called a reference dose (RfD), which EPA defines as: "An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark dose, with uncertainty factors generally applied to reflect limitations of the data used."

The basic idea behind the use of a reference dose approach is that it is scientifically inappropriate to assume that risk is proportional to dose at low doses (as is assumed for carcinogens), but instead, that a threshold exists below which toxic effects do not occur. Prior to the advent of benchmark dose methods, the reference dose was determined by reviewing the literature to determine either the highest exposure level at which no adverse effects were observed, a NOAEL, or the lowest level at which adverse effects were observed, a NOAEL, or the lowest level at which adverse effects were observed, a LOAEL. Whichever was selected was termed a "point of departure," and various safety and uncertainty factors were applied to derive a reference dose.

The benchmark dose approach is similar, except that a broader set of response data can be used to derive the point of departure. The details of the benchmark dose methodology are not described here, but Chapter 7 of the National Research Council's (NRC's) report (Committee on Toxicological Effects of Methylmercury, 2000) provides a detailed description. The benchmark dose method uses the statistical lower confidence limit of the dose that produces a predetermined change in response rate of an adverse effect in comparison to the background rate for the response.

#### A.2 Earlier Methylmercury RfDs

Prior to July 2001, the RfD for methylmercury was based on a poisoning event that occurred in Iraq when grain treated with a methylmercury fungicide was consumed. The initial analysis of the Iraqi poisoning focused on paresthesia, a neurological disorder that resembles prolonged "pins and needles." An RfD of 0.3  $\mu$ g/kg-day was derived based on this health endpoint. Later, EPA revised the RfD downward to 0.1  $\mu$ g/kg-day based on observed delays in the age of walking and talking in children born to Iraqi mothers exposed to methylmercury while pregnant.

For many toxicologists and others concerned with methylmercury exposures to the general population, use of the Iraqi poisoning event as the basis for the RfD was unsatisfactory for several reasons. The Iraqi poisoning reflected the short-term exposure to very high levels of methylmercury, in comparison to the situation of concern in the U.S. context – chronic exposures to low levels of methylmercury. In addition, there are uncertainties regarding the extent to which the health risks from consuming methylmercury in grain are representative of those from fish consumption. In the Iraqi event, the grain had been provided to a rural population experiencing famine. It was suggested that the underlying health status of the Iraqis and their limited dietary protein made this event a poor surrogate for chronic exposures to low levels of methylmercury

from fish consumption. Finally, the studies in Iraq were retrospective. While maternal exposure could be estimated from measurements of mercury in hair, other records such as the precise age of the children were lacking.

In 1997, EPA issued the *Mercury Study Report to Congress* and the *Utility Hazardous Air Pollutant Report to Congress*. While the prevailing RfD at the time of publication of these reports was that based on delayed walking and talking in Iraqi children, EPA noted that large studies were underway in the Faroe Islands and the Seychelles. *Faroe Islands (Committee on the Toxicological Effects of Methylmercury 2000).* These two studies were of populations chronically exposed to methylmercury, and designed to be carried out for an extended period. These studies would offer an improved basis for determining the health risks to the U.S. population from methylmercury.

#### A.3 The National Research Council Study

In 1999, Congress directed EPA to contract for a study of methylmercury toxicity with the NRC. This was done and the resultant report, cited above, was published in 2000. The committee charged with carrying out this study was faced with a difficult problem. While a number of studies had been done regarding methylmercury exposures to populations, two clearly stood out as more informative due to the large number of subjects involved, duration of follow-up, and the controls for confounding. These studies, one conducted in the Faroe Islands and the other in the Seychelles, produced inconsistent results; the Faroe study indicated a developmental effect from methylmercury to children exposed *in utero;* the Seychelles study did not. The Faroe study included slightly over 1,000 children. Maternal exposure was measured using both hair and cord blood. The Seychelles study population was over 700 children, and exposure was based on maternal hair.

In trying to understand why one study is positive and the other negative, many suggestions have been put forward. Initially, the children in the Seychelles study were assessed at younger ages and with less sensitive tests than in the Faroe study. These differences were suggested as reasons for the negative result, in comparison to the positive result in the Faroe study. However, subsequent follow-up studies in the Seychelles at later ages and with more sensitive developmental tests have not produced a positive result. One potentially significant difference between the two studies is that while exposures in the Seychelles were due to methylmercury consumed in fish, the major source of methylmercury in the Faroe study came from pilot whale meat. The Faroe study results were questioned due to the potential confounding by PCBs and other persistent organic pollutants. The National Research Council committee examined the potential for PCB confounding and found that "PCB exposure did not invalidate the use of the Faroe Islands study as the basis for risk assessment of methylmercury." In the committee's view, the fact that the methylmercury was concentrated in the whale meat while the PCBs were concentrated in blubber allowed for a distinction between the two pollutants. An additional theory proposed to explain why the Faroe and Seychelles studies produced conflicting results was that the exposures via fish consumption in the Seychelles were more uniform over time than the more episodic exposures due to whale consumption in the Faroe Islands. Absent a better mechanistic understanding of how methylmercury affects a developing fetus, the significance of continuous versus more episodic exposures remains speculative.

The committee also evaluated a study from New Zealand. In comparison to the Faroe Islands and Seychelles studies, the New Zealand study was much smaller. It included 57 sets of one "high" exposed child and 3 controls. The study used maternal hair concentration as the exposure metric. The results were positive, but very sensitive to one data point. The committee noted that this study had received less peer review than the other two. The overall evaluation of the three studies was:

The committee concludes that there do not appear to be any serious flaws in the design and conduct of the Seychelles, Faroe Islands, and New Zealand studies that would preclude their use in a risk assessment. However, because there is a large body of scientific evidence showing adverse neuron developmental effects, including well-designed epidemiological studies, the committee concludes that an RfD should not be derived from a study, such as the Seychelles study, that did not observe any associations with MeHg. ... The committee concludes that, given the strengths of the Faroe Islands study, it is the most appropriate study for deriving an RfD.

Although the committee was not charged with recommending an RfD, it did so based on benchmark dose calculations of the Faroe study results. The exposure metric recommended by the committee was cord blood, on the basis that fetal exposures were more closely linked to blood concentration than to maternal hair concentration and because the observed effect on test scores showed a stronger correlation with cord blood concentrations than with hair concentrations. Based on a 5% benchmark dose limit (that is, the lower 95% confidence limit on the exposure level that would produce a 5% increase in the incidence of abnormal test scores on the Boston Naming Test) a blood concentration of 58 parts per billion (ppb) methylmercury in blood was recommended as the point of departure. The committee noted that this blood concentration corresponded to a hair concentration of 12 parts per million (ppm). For comparison, the hair concentration previously used as a point of departure by EPA in the Iraqi-based RfD was 11 ppm. Despite the similarity of the calculated hair concentration based on the Faroe study to that from the Iraqi study, the committee recommended that the Iraqi study no longer be used as the scientific basis for the RfD.

In addition to the recommended point of departure of 58 ppb blood methylmercury, the committee recommended that an uncertainty factor of at least 10 be used, based on individual variability and on other health endpoints that had not been evaluated appropriately. The committee noted that the application of an uncertainty factor of 10 to their recommended point of departure, based on a one-compartment model to convert between blood concentration and methylmercury intake, would produce no change in the RfD, which would remain at 0.1  $\mu$ g/kg-day.

#### A.4 The Current RfD

EPA arrived at the RfD value that was recommended by the National Research Council, 0.1 µg/kg-day, but derived this value by a slightly different analysis from that used by the committee. There are two major differences between how EPA derived the RfD and the method used by the committee. The first is that EPA used an integrative analysis based on an evaluation of multiple test endpoints. While the test results used came mainly from the Faroe study, results from the New Zealand study also were included. Based on a recommendation from its peer review committee (US EPA 2000c), EPA included PCB-

adjusted benchmark dose limits, along with the unadjusted results and with results for the lowest PCB group in the Faroe data set. It was EPA's conclusion that these analyses pointed to an RfD of 0.1  $\mu$ g/kg-day if an uncertainty factor of 10 is used. The second significant change by EPA, in comparison to the committee's recommendation, concerns the basis for the uncertainty factor of 10. EPA used two uncertainty factors of 3 (which produce a combined uncertainty factor of 10 after rounding). One factor was to account for uncertainty and variability in estimating the relation between methylmercury intake and methylmercury in blood; the other was to account for pharmacodynamic variability and uncertainty. EPA did not apply the uncertainty factor for database limitations that had been recommended by the NRC committee. The full details of the derivation of the RfD are available at EPA's Integrated Risk Information System (IRIS) website.

A.5 What Population is to be Protected?

In its derivation of the RfD, EPA does not define explicitly the population groups to which it applies. However, because the derivation is based on studies of neurological effects due to *in utero* exposures, it is reasonable to conclude that the population to be protected are pregnant women or women who may become pregnant. Note: it is not known when, during the course of pregnancy, developmental effects from methylmercury occur. However, it is known that methylmercury is not rapidly removed from the body, so that a woman may have high blood methylmercury levels during pregnancy from exposures that occurred prior to pregnancy. The EPA methylmercury RfD discusses the rate at which mercury is eliminated from the body, and notes that the estimates for the clearance half-life for blood across five studies is quite variable, ranging from 32 to 189 days.

In its Criteria Document for Water Quality Criteria for Methylmercury (US EPA 2000g), EPA expresses a different viewpoint. In Chapter 5, Exposure Assessment, Section 5.2 addresses the question of the Population of Concern:

Methylmercury is a highly toxic contaminant that can cause a variety of adverse health effects. Toxicity has been observed in adults exposed through consumption of contaminated food. Toxic effects and subtle neuropsychological effects have been seen in children exposed *in utero* when their mothers consumed contaminated food while pregnant. The RfD (see section 4) is based on changes in neuropsychological measures in children exposed *in utero*. The choice was made to use a developmental endpoint, as this appeared to be the most sensitive indicator of a methylmercury effect. As discussed in section 4, there is concern that other less-studied effects may occur at lower doses. There is also concern (based on recent reports on the Minamata, Japan, population) that exposure *in utero* or in childhood could result in subtle impairments that would not be detectable until middle age or older.

The RfD for methylmercury was not calculated to be a developmental RfD only. It is intended to serve as a level of exposure without expectation of adverse effects when that exposure is encountered on a daily basis for a lifetime.

In the studies on subtle neuropsychological effects in children published so far, there has been no definitive separation of prenatal and postnatal exposure that would permit dose-response modeling. That is, there are currently no data that would support the derivation of a child RfD versus a general population RfD.

Therefore, the population at risk evaluated for the methylmercury criterion is adults in the general population, not only the developing fetus or child.

This description is somewhat at odds with the RfD itself, which lists the critical effect on which the RfD is based as "developmental neuropsychological impairment." The methylmercury RfD does not explicitly address which population it applies to; but, the point mentioned above regarding continuing exposures to children exposed *in utero* is not mentioned in the RfD or in the NRC report on which it is largely based.

Nothing in the derivation of the RfD suggests that it is applicable to males of any age or to women not of childbearing age. However, it is the case that the children in the Faroe study received continuing exposures after birth, so that the Faroe Islands, Seychelles, and New Zealand studies are not purely developmental studies. It is suggestive that the authors of these studies apparently thought that the *in utero* exposures were the determinants of developmental effects, if any. No effort was made to estimate childhood exposures and to integrate them with *in utero* exposures.

The intent of EPA's application of the RfD to all adults and children is clearly to assure protection for all members of the population. But, a potential consequence of applying the RfD to everyone is that the particular concern with the protection of pregnant women or women who could become pregnant will be lost. As the states and tribes implement the water quality criterion, it is important that the scientific basis for the RfD not be overlooked, and that the information regarding health risks from methylmercury exposures through consumption of freshwater fish be targeted, at least to a degree, towards women who are or may become pregnant.

# Appendix B. Use Of Weighted BAF To Derive Ambient Water Quality Criteria For The Protection Of Human Health

EPA finalized its methodology for deriving ambient water quality criteria for the protection of human health in October, 2000 (US EPA 2000a). The methodology uses the following formula to calculate the water quality target (WQT):

where

WQT is the water quality target (ng/L) BAF is the bioaccumulation factor (L/kg), and Fraction MeHg is the ratio of methyl to total mercury (dimensionless).

The TMDL document for the Savannah River (EPA 2000f) states that EPA Region 4 used the Agency's final human health based methodology to calculate the appropriate water column concentration. Despite this claim, the guidelines provided in this methodology were not adhered to as discussed in the following paragraphs.

*Fish Consumption Rate* – EPA methodology recommended four methods to calculate the fish intake rate. The <u>first and most preferred method</u> is to use consumption data for local watersheds that are representative of the population. If this survey is not available, <u>the second preference</u> is to use existing fish intake surveys that reflect similar geography and population groups. If this is not available, the <u>third preference</u> is to use national food consumption surveys for different population groups. The <u>fourth and least preferred</u> <u>method</u> is to use EPA's default consumption rate of 17.5 g/day. In addition, the fish consumption rate should be calculated on a trophic level basis (as described below).

BAF and Trophic Level Considerations – EPA's methodology document further recommends that "bioaccumulation factors (BAFs) be determined and applied on a trophic level-specific basis" (Page 5-5 in methodology document). The document recommends the use of the following weighting function:

$$\sum_{i=2}^{4} FI_i \times BAF_i$$
 (B-2)

where

Fl<sub>i</sub> is the fish consumption of trophic level 'i' fish, and BAF<sub>i</sub> is the bioaccumulation factor for trophic level 'i'.

EPA Region 4 used only trophic level four fish and associated bioaccumulation factors in its analysis.
*Fraction Methylmercury* – The methodology document states that "different forms of many inorganic and organomettalic chemicals (*e.g., methylmercury*) may inter-convert once released to the aquatic environment (in this case mercury to methylmercury)... In these cases, sufficient data should be available to enable conversion between total concentrations and the other more bioavailable (in this case MeHg) forms in water." EPA's data did not demonstrate reliably the relationship between total and methylmercury. Neither in EPA's TMDL document nor in the literature is there sufficient information to predict methylmercury from total mercury concentrations in water.

Thus, in our opinion, EPA Region 4 misapplied this formula to arrive at the water quality target by using a fish consumption rate of 17.5 g/day together with the bioaccumulation factor measured in the Savannah River for largemouth bass and other trophic level 4 fish. The implicit assumption that 17.5 gram/day is the fish consumption rate for largemouth bass and trophic level 4 fish taken from the Savannah River is invalid.

#### Weighted BAF Approach

According to EPA's guidance document (US EPA 2000a), in order to do the WQT calculation properly, a weighted bioaccumulation factor must be utilized, taking into account the other species of fish harvested and estimates of the bioaccumulation factors for fish of that species and size. As shown above, the weighted bioaccumulation factor is the sum of the products of the bioaccumulation factor for each fish species and the fraction of that species consumed. An upper limit on this number is the percentage of largemouth bass actually harvested by weight. This weighted bioaccumulation factor must be used in conjunction with an accurate estimate of fish consumption.

On page 34 of the Savannah River TMDL document, EPA states that "Trophic level four fish (largemouth bass) were targeted in the collection because they represent a major portion of the fish size that is caught and kept by anglers and consumed as a food source." This statement is incorrect. Species harvest data from the freshwater portion of the Savannah River as a percentage of the total harvest on a number and weight basis are excerpted from this document and are shown in the following table (Schmidt and Hornsby 1985).

Species	Percent of total	Percent of total	Average Weight		
	harvest by number	harvest by weight	(kg)		
Striped bass	0.2	3.9	4.21		
Striped x white	0.3	2.1	1.68		
bass					
Bluegill	24.1	13.6	0.13		
Redbreast sunfish	27.2	16.2	0.13		
Warmouth	7.3	4.8	0.15		
Redear sunfish	4.4	3.9	0.20		
Spotted sunfish	1.1	0.4	0.09		
Largemouth bass	3.2	8.3	0.58		
Crappie spp.	8.0	7.2	0.2		
Yellow perch	3.0	1.9	0.14		
Channel catfish	4.2	6.1	0.32		
White catfish	2.1	3.1	0.33		
Bullhead spp.	8.2	5.5	0.15		
Shad	1.7	11.0	1.42		
Chain pickerel	0.9	1.8	0.43		
Others <sup>17</sup>	4.1	10.2	0.55		
Total	100.0	100.0	0.22		

The data in this table clearly shows that trophic level four fish including largemouth bass, chain pickerel, and bowfin do not represent a major portion of the fish caught and kept by anglers and consumed as a food source. Largemouth bass and chain pickerel make up only 10% of the harvest by weight. Adding a generous estimate of the bowfin harvested by weight, the three species make up less than 15% by weight of the total harvest.

Without justification, EPA Region 4 designated a trophic level four fish of 315 mm length as "representative of the size and age fish that is most likely consumed." This statement also is incorrect and misleading. Regression of EPA's data (predominantly largemouth bass) on fish length and weight show that a 315 mm fish in their database corresponds to a fish of approximately 1.2 lbs. or 0.54 kg. A fish of 0.54 kg is close to the average weight of largemouth bass harvested in the Savannah River (0.58 kg). However, the average size fish harvested from the Savannah River is only 0.22 kg, as shown above. Furthermore, the catch is heavily weighted toward species such as sunfish that tend to have lower bioaccumulation factors (BAFs) than trophic level four fish such as largemouth bass.

In general, other species have lower mercury body burdens (and therefore lower BAFs) than do largemouth bass. The following table shows average composite (1993-1997) fish tissue mercury concentrations from the Savannah River in several fish species.

<sup>&</sup>lt;sup>17</sup> Bowfin comprises 19 percent by number of fish in the "other" category or 1.9% of the total catch by number.

Species	Hg (mg/kg)	# of Composites
Largemouth bass and	0.48	24
bowfin		
Spotted sucker, sucker,	0.21	9
and red drum		
Redbreast, redear sunfish	0.12	6
Channel, white catfish	0.17	15

Assuming that all species have been exposed to the same mercury concentrations during this period of time, average bioaccumulation factors for the various species can be assumed to be proportional to the fish tissue concentrations in each species. Therefore, approximate bioaccumulation factors for each species can be calculated using the ratio of the species tissue concentration to the tissue concentration in largemouth bass and bowfin. Assuming EPA's BAF of 4,000,000 for largemouth bass and bowfin, the computed bioaccumulation factors are shown below:

Species	Tissue conc. (species) / Tissue conc. (LMB, bowfin)	% of Species and Similar Species Harvested	BAF (L/kg)
Largemouth	1.0	15	4,000,000
bass, bowfin			
Sucker,	0.44	12 <sup>18</sup>	1,760,000
spotted			
sucker, red			
drum			
Redbreast,	0.25	<b>48</b> <sup>19</sup>	1,000,000
redear sunfish			
Channel, white	0.35	15 <sup>20</sup>	1,400,000
catfish			
Other	-	10	
Total		100	

Using the bioaccumulation factors and weights in the above table (and normalizing the weights to account for the 10% missing species), an estimate of the species-weighted bioaccumulation factor for the Savannah River is 1,650,000 L/kg. This number is lower than the BAF of 4,000,000 used by EPA for the Savannah River by a factor of 2.4.

Using this weighted bioaccumulation factor in the WQT formula results in a value for the water quality target of 6.9 ng/L.

EPA may be interested in the validity of the average fish tissue mercury concentrations for the species composites shown above. As validation, we offer the following additional observations. Data from the State of South Carolina for individual fish shows that the average tissue concentration in largemouth bass is 0.42 mg/kg and in bowfin 0.43 mg/kg. These correspond closely with the GA numbers for trophic level four fish shown above. It is also of interest that the EPA's trophic level four fish tissue concentrations

<sup>&</sup>lt;sup>18</sup> Includes shad

<sup>&</sup>lt;sup>19</sup> Includes bluegill, warmouth, spotted sunfish, crappie, and yellow perch

<sup>&</sup>lt;sup>20</sup> Includes bullhead

measured in its 2000 sampling program on the Savannah River average 0.482 mg/kg, almost identical to the average derived from the Georgia Environmental Protection Department's (EPD's) data. Individual catfish caught and tested by the State of South Carolina averaged 0.14 mg/kg (compare to 0.17 mg/kg from the Georgia data), and individual redbreast sunfish averaged 0.13 mg/kg and redear sunfish 0.16 mg/kg (compare to 0.12 in the Georgia data)<sup>21</sup>.

<sup>&</sup>lt;sup>21</sup> Catfish, redbreast sunfish and redear sunfish data from South Carolina have a high number of non-detects. Half the value of the detection limit was used to compute the averages shown here.

					FISH SPECIES	5						
		Tro	phic Level 3	Fish				Trophic L	evel 4 Fish			
	Yellow	Sunfish	Brown	Channel	Cut-Throat	Brown Trout	Small-	Large-	Walleye	Chain	Bass	Comment
	Perch		Bullhead	Catfish	Trout		mouth	mouth		Pickerel		
STUDY							Bass	Bass				
Suns & Hitchin 1990	0.031 - 0.233											Yearling Perch; 16 Canadian Shield Lakes
												1-7-Year old Yellow Perch & Golden
Watras et al 1998	0.019 - 0.544											Shiners15 small lakes, Vilas Co., WI
Forcella 1994	0.025 - 0.200							0.046 0.090		0.010 1.050		Sevenesh Biver, GA and tributaries, 2000
Brumbaugh et al 2000							0 510 -1 100	0.246 - 3.960	0 660 - 0 700	0.010 - 1.255	0 640 - 3 360	Nationwide study
Brumbaugh et al 2000							0.510 1.100	0.000 2.170	0.000 0.700	0.000 0.010	0.040 0.000	2-year old Yellow Perch: 10 No. WI
Cope et al 1990	0.030 - 0.290											seepage lakes
Serdar et al 2001	0.047 - 0.869		0.032 - 0.785		0.032 - 0.198		0.100 - 1.30	0				Data from Whatcom Lake, WA; single year
Armstrong et al 1995		0.290 - 0.820		0.010 - 1.190				0.210 - 2.69			0.270 - 2.870	Data from Arkansas rivers and reservoirs
												Data from 7 northern California reservoirs
May et al 2000				0.160 - 0.750			0.500 - 0.96	0 0.200 - 1.200			0.580 - 1.500	and 4 streams
606		0.000 4.000		0.000 4.400		0.040 0.000		0.000 0.000				tributorios: 1006 1008
383		0.330 - 1.000		0.330 - 1.430		0.040 - 0.390		0.330 - 2.820				Data from six blackwater So. Georgia
EPA Region 4 2001		0.040 - 1.000	0 390 - 0 820					0 260 - 1 770		0 390 - 0 960		rivers: 2000-2001
		0.040 1.000	0.000 0.020					0.200 1.770		0.000 0.000		11010, 2000 2001
Range in Fish			0.010 - 1.430	)				0.040	- 3.980			
5												US EPA's National survey of mercury
Range in Fish; EPA 1999	0.010 - 2.140	0.001 - 1.680		0.001 - 2.570			0.008 - 3.34	0 0.001 - 8.940	0.008 - 3.000			concentrations in fish
												US EPA's National survey of mercury
Est. 25th - 90th Percentile		0.050 - 0.380		0.050 - 0.400				0.220 - 1.150	0.180 - 0.680			concentrations in fish

	All Fish												
Mean	C۷												
0.71	48												48
	By Location												
AL&I	D	BDC	FMC	SR17	S301	L-L	LTRC	PAR	P-B	SC	SRSB	UTR	
Mean	CV	Mean CV	Mean CV	Mean CV	Mean CV	Mean CV	Mean CV	Mean CV	Mean CV	Mean CV	Mean CV	Mean CV	
0.6		0.67	0.61	0.55	0.59	0.86	0.8	0.93	0.92	0.78	0.7	0.66	
	34	47	34	37	37	34	53	53	42	47	50	37	42
Bass	By Species												
Mean	CV	Mean CV	Mean CV	Mean CV	Mean CV								
0.89	0.	0.49	0.52	0.52	0.71	4							
	40	36	32	34	42								36
			_		By Spec	ies by Lo	ocation		_	_			
AL&I	D	BDC	FMC	SR17	S301	L-L	LTRC	PAR	P-B	SC	SRSB	UTR	
Bass	29	39	26	26	27	30	51	17	39	28	27	36	
Bowilh	17	30	27		32		20	26		52	17		
Catfish		32 31	13	29	28		20			24 67	26	30	
Panfish	39	51	21	5	20		41	15		56	20	22	
	30			·									30

#### Location Key

AL&D = Augusta Lock and Dam BDC = Beaver Dam Creek FMC = Four Mile Creek SR17 = Savannah River @ Highway 17 S301 = Savannah River @ Highway 301 L-L = L Lake LTRC = Lower Three Runs Creek PAR = PAR Pond P-B = Pond B SC = Steel Creek SRSB = Savannah River @ Stokes Bluff UTR = Upper Three Runs Creek

Data Source: Savanah River Site, Environmental Reports (1996, 1997, 1998)

									ŀ	All Fish									AVG
Mean	CV																		
0.49	84	-																	84
SRCH	D	нс	;	SRH	IC	Bu	С	SRB	uC	UTR	SRU	JTR	LTR	SRLTR	BrC	SRE	BrC	SRCLY	C
Mean	CV	Mean	CV	Mean	CV	Mean	CV	Mean	CV	Mean CV	Mean	CV	Mean CV	Mean CV	Mean CV	Mean	CV	Mean C	V
0.25		0.26		0.07		0.3		0.32		0.8	0.18		1.1	0.2	0.5	0.42		0.6	
	45		54		29		37		72	40		39	21	58	50		86	7	2
	By Location (Cont.)																		
EC		SRE	C	TG	F	TG	E												_
Mean	Cν	Mean	CV	Mean	CV	Mean	CV												_
1.27	40	0.00	~ ~	0.41		0.39													54
	42		60		64		23												51
									Ву	Species	5								
Bass	;	Striped	Bass	Bow	fin														
Mean	CV	Mean	CV	Mean	CV														
0.36		0.49		0.96															
	87		36		48														
																			57

#### Location Key

SRCHD = Savannah River below Clark Hill Dam HC = Horse Creek SRHC = Savanah River below Horse Creek BuC = Butler Creek SRBuC = Savannah River below Butler Creek UTR = Upper Three Runs Creek SRUTR = Savannah River below Upper Three Runs Creek LTR = Lower Three Runs Creek SRLTR = Savannah River below Lower Three Runs Creek BrC = Brier Creek SRBrC = Savannah River below Brier Creek SRCLYO = Savannah River @ Clyo, GA EC = Ebenezer Creek SREC = Savannah River below Ebenezer Creek TGF = Tide Gate, Freshwater TGE = Tide Gate, Estuary

Data Source: US EPA (2000), Savannah River TMDL Administrative Record



Location Key

F=Felsenthal National Wildlife Refuge C=Calion Lock and Dam W=Lake Winona S=Shepards Springs Lake

Data Source: Mercury in Arkansas: 1993-1994 Biennium Report

	Tota	l Hg	Dissolv	/ed Hg	Total I	MeHg	Dissolved MeHg		
	Temporal Spatial		Temporal	Spatial	Temporal	Spatial	Temporal	Spatial	
Mean (ng/L)	589		197		0.332		0.157		
Mean CV	47	60	53	145	56	70	51	64	
Range	17-93	39-103	25-138	114-188	35-90	54-121	22-88	46-91	

 Table 4.5. Coefficients of Variation (CV) for water samples collecetd from East Fork Poplar Creek, TN

# Mercury Source Control & Pollution Prevention Program Evaluation

**Final Report** 

Prepared for: Association of Metropolitan Sewerage Agencies (AMSA) (Under Grant from U.S. Environmental Protection Agency)

Prepared by:





#### DISCLAIMER

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Appendix D. Sensitivity Analysis

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## Introduction

The effects of mercury exposure on human health and wildlife are driving a number of efforts to significantly reduce the level of this toxic, persistent, and bioaccumulative metal in the environment. Exposure to mercury, a neurotoxin, affects the brain and nervous system. Young children and developing fetuses are most susceptible to its harmful effects. Long-term exposure may cause, among other things, a loss of physical coordination and mental retardation. The consumption of fish from waters contaminated with mercury offers the greatest risk of exposure to this pollutant. [TriTAC, 2001].

Mercury enters waterbodies through several pathways including air deposition (from combustion and incineration processes), urban runoff, wastewater discharges, geothermal discharges, mine site runoff, and contaminated sediments.

Increased monitoring of mercury in the water column and fish tissue and the application of more stringent standards has led to increasingly stringent mercury effluent limits in NPDES permits. Some of the standards that have been used or proposed are listed in Table 1.

Table 1. Mercury Water Quanty Criter	14
Basis of Criteria	ng/L
California Toxics Rule Saltwater Criterion	25
EPA Fish Tissue Methyl Mercury-based Criterion (Rivers & Streams)	17-18 <sup>1</sup>
EPA Fish Tissue Methyl Mercury-based Criterion (Lakes)	7.5-7.8 <sup>1</sup>
Great Lakes Initiative Human Health Criterion	3.1
Great Lakes Initiative Wildlife Criterion	1.3
Proposed Maine Freshwater Chronic Criterion	0.2

#### Table 1. Mercury Water Quality Criteria

Currently, approximately 6% (253 of 4307) of the major publicly owned treatment works (POTWs) have NPDES permits with mercury effluent limits and approximately 10% of the major POTWs (423 of 4307) have monitoring requirements (Morris, 2001). As more monitoring for mercury is conducted, the number of agencies with effluent limits is likely to significantly increase. Of the agencies with limits, several (particularly in the Great Lakes region) have limits based on the Great Lakes Initiative (GLI) Wildlife Criterion (i.e., 1.3 ng/L) and have had difficulty meeting these limits (EPA, 2001).

In order to comply with permit requirements, POTWs with effluent limits for mercury have investigated a variety of strategies, including non-regulatory approaches such as pollution

<sup>1</sup> These are projected criteria for total mercury that have been calculated from the national fish tissue residue criteria for methylmercury using, as default values, draft bioaccumulation factors, trophic level-specific fish consumption rates, and dissolved methyl-to-total mercury translators.

prevention and source control, in an effort to achieve mercury reductions. National efforts to reduce mercury releases to the environment have already used source control and pollution prevention to target incineration of medical and dental wastes, disposal of consumer products (i.e., fever thermometers, thermostats, switches, fluorescent light bulbs) and dental office wastewater discharges.

In addition to source control and pollution prevention programs, mercury has also been the target of legislation. Legislation to restrict mercury use in consumer products and in certain other applications has been introduced at the federal level as well as in many states throughout the country. Legislation has been proposed that prohibits the sale or supply of mercury fever thermometers (except by prescription), novelty items and automobile switches as well as prohibiting purchases of mercury by schools. Some bills propose the immediate removal of mercury switches from automobiles and provide technical assistance to wrecking yards to remove mercury switches. Yet another bill prohibits improper disposal of mercury containing products and requires POTWs to perform wastewater monitoring, source identification and pollution prevention. There is also a provision requiring that mercury containment traps be installed for facilities that have the potential to discharge trace amounts of mercury to the sewer system. Many states are creating task forces to come up with recommendations on how to regulate mercury as a solid and hazardous waste.

While pollution prevention and source control are effective tools for reducing the amount of a pollutant entering the environment, several factors influence a POTW's ability to achieve mercury reductions and permit compliance using pollution prevention and source control. These factors include:

- Initial influent mercury levels;
- Percentage of the influent loading that can be attributed to specific sources;
- Ability of the POTW to control a particular source;
- Potential effectiveness and cost of the source control strategies employed;
- Form of mercury present in the influent (i.e., particulate vs. dissolved);
- Treatment plant removal efficiencies at varying influent concentrations; and
- Final effluent limit that must be achieved and corresponding reduction needed to achieve this limit.

The purpose of this project was to:

- Determine the extent to which pollution prevention and source control programs can achieve measurable reductions of mercury in POTW influent, and if these reductions will enable POTWs to comply with new, lower effluent limits based on the criteria listed in Table 1. (Note: The term pollution prevention program, as used in this report, refers to a source control program that uses only voluntary approaches); and
- 2. Identify the beneficial impacts of wastewater source control on other pathways by which mercury enters the environment.

The following steps were taken to complete this assessment:

- Estimate mercury reduction in influent achievable through source control;
- Assess ability of POTW to comply with effluent limits based on these influent reductions;
- Compare impact of implementing source control programs (cost) with impact of additional POTW treatment costs; and
- Identify benefits of source control programs in addition to impacts on wastewater.

The procedure used and the results of this assessment are described in the following sections.

*Procedure.* This section describes the process, the assumptions and the data sources used in the analysis.

*Results.* The results of the analysis are presented with respect to estimated mercury influent loadings for each plant, reductions that may be achievable through pollution prevention, resulting effluent mercury levels and potential for each case study candidate to comply with future effluent limits. The impacts of the various assumptions made are also discussed in this section.

*Findings*. The implications of the results with respect to the potential effectiveness of mercury pollution prevention programs and regulatory impacts are discussed. The impacts on other media in addition to water are also considered. Limitations of the study are presented.

*Conclusions and Recommendations.* Overall conclusions are summarized. Recommendations for source control programs are presented. Areas requiring future study are identified.

## Procedure

A flow chart of the process used to reach final effluent concentrations based on pollution prevention activities can be found in Figure 1. The basic steps of this process included:

- Selection of Case Studies
- Source Identification
- Source Load Calculation
- Reduction Estimate
- Resulting Influent, Effluent and Biosolids Loads and Concentrations
- Comparison to Effluent Limits
- Cost of Compliance

These process steps are described in detail below.

#### Selection of Case Studies

Initial outreach to POTWs was based on plant size and geographic location. To encompass a range of possible mercury sources and concentrations, different size plants, spread throughout the country, were contacted. Spreadsheets were e-mailed to each agency asking for information such as the number of households, influent/effluent concentrations and number of dental offices

in their service area (See "Plant Data Spreadsheet" in Appendix A). Several agencies provided data and information about their plants and service areas, some of which is shown in Table 2, below. The data entered into the Plant Data Spreadsheet were linked to a second spreadsheet which used source values from previous studies to calculate loadings (grams/day) for each identified source.

#### Figure 1. Flow Chart of Processes Used



*Mercury Source Control and Pollution Prevention Program Evaluation Final Report* 

Table 2. POTW Data

POTW		Community Size	Ave. Op. Size (MGD)	Average Inf. (ppt)	# Influent Samples	Average Eff. (ppt)	# Effluent Samples	Average Biosolids (g/day)	# Biosolid Samples	Analytical Method	MDL (ppt)	Time Period	% Non- Detect (effluent)
Massachusetts Water Resource Authority (MWRA)	МА	2.5 M	375	260	12	30	12	340		245.1	10	1999- 2000	
Hampton Road Sanitation District (HRSD)*	VA	1.5 M	157	29-292	43	<5-29.5	36	5.7-21.1	133	245.7	5 QL	2000- 2001	86%*
Sacramento Regional County Sanitation District (SRCSD)	CA	1.1 M	157	227	105	9	116	113	164	1631	0.06	1998- 2000	0%
Northeast Ohio Regional Sewer District - Easterly (NEORSD -e)		401,167	104.1	143	19	3.56	19	55	19				0%
Northeast Ohio Regional Sewer District - Southerly (NEORSD-s)	он	597,936	109.5	323	10	3.17	11	144	366	1631	0.5	2000	0%
Northeast Ohio Regional Sewer District - Westerly (NFOR SD-w)		123,170	31.2	113	7	3.11	11	16	366				0%
San Francisco - Southeast Plant	CA	564,744	65	414	23	21	50	< 0.323	2	1631	25	2000	0%
San Francisco - Oceanside Plant	CA	224,033	17.6	237	12	51	18	< 0.097	2	1001		2000	0%
Western Lake Superior Sanitary District (WLSSD)	MN	95,000	39	106	366	4.7	353	16.3	47	245.1	5	2000	58%
Palo Alto Regional Water Quality Control Plant	CA	226,000	28	219	34	5.5	24	25.2		1631	10	1999- 2000	50%
Green Bay Metro Sewerage District (GBMSD)	WI	180,900	28	104	12	<7	12	18.9	40	245.7	7	2000	100%
Portland Water District - Portland Plant	ME	60,000	16.4	101	1	14	8	8.47		1631	0.2	2000	0%
Lewiston-Auburn WPCA	ME	50,000	12.2	70	4	5	11	10.15	39	1631	0.2	1999- 2000	0%
Novato Sanitation District (NSD)	CA	34,190	4.4	593	30	22.6	34			1631	10	1998- 2000	0%
Portland Water District - Westbrook Plant	ME	15,000	2.51	281	3	6.9	7	1.51		1631	0.2	2000	0%

\*The data in Table 2 for the Hampton Roads Sanitation District were changed in July 2002 to more accurately reflect actual monitoring information. Note that the value in the column for Method Detection Level (MDL) is a Quantitation Level (QL) not an MDL. Also, the % Non Detect value is the percent not quantifiable, rather than not detectable. The "effluent" values were obtained at the end of HRSD's chlorine contact tanks, which is not the official effluent sampling site.

To develop reasonable load reduction calculations, it was important to use data that accurately accounted for a majority of the mercury moving through each plant. Therefore, mass balance closures (influent = effluent + biosolids) were determined for each agency to assess the quality of available data. Influent, effluent and biosolids loads were determined based on flow and concentration data provided by each agency. Agencies used for the full calculation were selected based on the following criteria:

- Number of influent and effluent samples reported
- Analytical method and detection limits
- Mass balance closure
- Availability of all requested information.

## Source Identification and Data Sources

Many studies have been performed that attempt to identify sources of mercury from commercial, residential and industrial activities. In addition, research has been conducted on the effectiveness of pollution prevention and source control programs. Information on sources of mercury and effectiveness of pollution prevention was collected from various reports and Internet sites. In most cases, data obtained were averaged to obtain representative mercury concentrations and source flow data. A variety of commercial, industrial and residential sources were considered. Stormwater inflow and septage waste were also considered for agencies who provided data on these sources. The mercury data used for source loading calculations, and an explanation of how the final values were calculated can be found in Appendix B. Two of the most significant sources were dental office discharges and human waste associated with amalgam fillings. Literature values for these two sources were highly variable and based on several assumptions. Therefore, a sensitivity analysis (Appendix D) was conducted to assess the impact of varying these two values. By varying the dental and human waste values it was possible to get a sense of how influential the numbers used for these sources were on reduction estimates, mercury concentrations, compliance, and project costs. Dental and human waste loading data were chosen as discussed below.

#### **Dental Loading**

Mercury levels measured in dental wastewater were used to estimate loading contributions from dental offices to treatment plant influent. Several studies were available in which wastewater concentrations, water flow and consumption rates, and number of dentists had been measured [Rourke, 2000; SFWPPP, 1993; Barruci *et al.*, 1992; NEORSD, 1997]. Because there is no way to conclude that any one of these studies is better then another, the data were treated equally. An unweighted average of the data from these studies resulted in a dental loading value of 56 mg/dentist/day as shown in Table 3. Other studies measuring mercury discharges from dentists that were considered include those by Drummond et al., Cailas et al. and Arenholt-Bindslev and Larsen (Table 4) and Metropolitan Council Environmental Services (MCES). The differences between the values measured in Tables 3 and 4 are discussed below.

Table 5. Data Used for Calculation of Dental Loading Value				
Barruci et al., 1992	35 mg/dentist/day	24 samples from 3 buildings		
SFWPPP, 1993	46 mg/dentist/day	56 samples from 9 buildings		

Table 3. Data Used for Calculation of Dental Loading Value

Rourke, 2000	98 mg/dentist/day	114 samples at 6 buildings	
NEORSD, 1997	44 mg/dentist/day	37 samples at 5 facilities	
AVERAGE	56 mg/dentist/day (0.056 g/dentist/day)		

 Table 4. Mercury Loadings in Dental Clinic Vacuum System Wastewater

All data is	Passing Chairside Trap	Passing Chairside Trap	Discharged	Discharged
given as:	(per chair)	(per chair)	(per dentist)	(per dentist) (2)
mg Hg/day	soluble + solids	settled solids(1)	without amalgam removal equipment	without amalgam removal equipment
Mean	612	773	250	234
Median	499	522		
Ν	58	66	10	275 (3)
Maximum		3298	842	1293
Minimum		20	65	8
Std. Dev.	529	733		
Reference:	Cailas, et al. (1994)	Drummond, et al. (1995)	Arenholt-Bindslev and Larsen (1996)	Berglund (2001)

 Supernatant passing chair had low mercury amount relative to solids, and also variable amount. Drummond also measured the amount of mercury in solids retained in chairside traps.
 The median value was \$10 mg/abais/day (N = 57, Std. Day, = 1032)

The median value was 819 mg/chair/day (N = 57, Std. Dev. = 1032).

(2) Data for seven clinics, all operated with a chairside trap. Five operated with a vacuum filter, and two without a vacuum filter.

(3) Some samples of wastewater and waste solids were collected over numerous days. Therefore, the "N", or number of samples, is less than 275. However, the units for the data is "per day", and the number of days of sample collection was 275 days.

The values listed in Table 4 are based on samples taken in the dental office. MCES (WEF, 1999) estimated that half of the mercury passing the chairside traps would be captured in a vacuum filter, commonly used with liquid-ring vacuum pumps. The other half, or 250-261 mg/dentist/day (WEF, 1999) would be discharged from the clinic vacuum system and mixed in with the clinic's other wastewater. A recent study by MCES estimated a dental loading contribution of 120 mg/dentist/day to the influent of two treatment plants (Anderson, 2001). This was based on a back-calculation from measured reductions in biosolids mercury levels and estimated grit removal rates resulting from installing amalgam removal equipment at all dental clinics in two treatment plant service areas (the result of 120 mg calculated out the same for each of the two service areas). A second study recently completed by MCES found a variable loading

rate from dentists, yet with a similar average loading rate of 234 mg/dentist/day (Berglund, 2001), as compared to the other data in Table 4.

The basis for the calculations in this report is 56 mg/dentist/day (0.056 g/dentist/day). In the sensitivity analysis, loading values greater than 56 mg/dentist/day will be used, up to 150 mg/dentist/day (with the understanding that the loadings may be higher than 56 mg/dentist/day based on data from Cailas, et al., Drummond et al., Arenholt-Bindslev & Larsen, and MCES). The measurements leading to the average of 56 mg/dentist/day may be lower than data in Table 4 and lower than the 250-261 mg/dentist/day reported by the 1999 WEF monograph due to issues with:

- Sampling location and amount of solids suspended in liquid fraction; and
- Subsampling prior to analysis and digestion methods of subsample.

Some portion of the amalgam that goes down the drain will settle in the collection system and leach back into the liquid fraction (which will contain particulate and dissolved mercury) over time. While there is a considerable amount of uncertainty regarding the fate and transport of solid amalgam in sewer lines, this settling could explain the difference in concentrations measured in the collection system (Table 3) and the concentrations measured in the dental office (Table 4). Another possible factor contributing to the differences in the values listed in Tables 3 and 4 is the digestion method used as part of the sample analysis. The digestion process used for wastewater in Methods 245 and 1631 is appropriate for samples with low solids (i.e., values listed in Table 3). However, a more aggressive digestion method is used for high solids samples and may account for the higher mercury levels shown in Table 4.

It was assumed that the samples taken in the laterals leaving the dental offices (Table 3) represent the best estimate of the mercury actually leaving the dental office and the mercury leaching back into the liquid fraction at a given snapshot in time that will ultimately reach the treatment plant headworks. Therefore, 56 mg/dentist/day offers the best representation of the mercury that enters the treatment plant. Other viewpoints on this issue are addressed in Appendix C: Response to Comments.

#### Human Amalgam Waste Loading

In the case of human waste loadings associated with amalgam fillings, wastewater data was not readily available. Instead, the analysis used a calculated loading designed to best represent a typical U.S. population. A number of existing studies were reviewed to formulate the loading for this analysis. A Canadian study compiled data from a variety of sources and attempted to account for the relationship between number of fillings and human waste-amalgam mercury loadings. The resulting number was 11  $\mu$ g/person/day [O'Conner Associates, 2000]. However, this was based on data averaging the number of fillings per person in Canada in the 1970's. Another study, done by Barron (2001a, 2001b), found that the average number of amalgam surfaces is 16.6 per person (based upon Hyman data for the 1990 United States census). From this, the daily average mercury waste (urine + feces) is in the range of 27-39  $\mu$ g/day/patient.

'Patient' refers only to adults with amalgams. Restated, for all people beyond just those who have amalgams, the overall average number of amalgam surfaces is 10.8 per person. Therefore, the daily average loading is in the range of 17 to 26  $\mu$ g/person/day. 'Person' here means all adults (>20 years), including those with and without amalgam fillings. The estimate based upon the Hyman data for fillings per person gives the high end of the above two ranges. The lower estimate is found by using Skare's (1995) average and low values (Table 5). Skare's curve fit was not used because the data included individual(s) with very high amalgam counts.

					0
	Surfaces	U-Hg	F-Hg	Total Hg	Units
Ave	40	1.7	64	65.7	µg/day/patient
Low	18	1.4	27	28.4	µg/day/patient

Table 5.	<b>Barron's Estimates</b>	s Applied to Skare'	's Average and Lo	w Values
I GOIC CI		supplied to share	b il vei age ana 110	

These values imply mercury waste loads of 1.64 (65.7÷40) and 1.58 (28.4÷18)  $\mu$ g/day PER AMALGAM SURFACE, respectively. The Barron estimate (2001b) uses 1.60  $\mu$ g/day for this parameter. Doing so produces a human mercury waste result of 26.5  $\mu$ g/day/adult 'patient', which is equivalent to an overall average of 17.2  $\mu$ g/day/adult 'person'. Table 6 summarizes human waste values calculated in the studies cited. Table 7 provides details of how these values were calculated.

Table	Table 0. Human waste Mercury Studies Cited				
Peference	Human Waste	Amalgam	µg Hg∕		
Reference	(µg/person/day)	Surfaces	surface /day		
Skoro	49.3	40	1.64		
Skare	21.3	18	1.58		
Barron	17.2	10.8	1.60		
O'Conner	11.4	7.6	1.50		

 Table 6. Human Waste Mercury Studies Cited

The value calculated by Barron, 17.2  $\mu$ g/day/person, was used because it appears to be the most representative of the U.S. population. This number accounts for all people; the fact that some people have amalgam fillings and some don't, has been factored into the 17.2  $\mu$ g/day/person value.

	Barron (2001b)	O'Connor (2000)	Skare (1995a)	Skare (1995b)	AMSA (2000)
	[Revised] [1,2]	[Table 4.2] [3]	[Table 1 - low]	[Table 1 - mid]	[Page 11]
Par A dult Parson (including just those with amalgan	a fillinga)				
<u>rei Addit Ferson (including just mose with amaigan</u>	<u>10.42</u>				
Total Filling Surfaces/person	18.43	• • •	• • •	• • •	• • •
Pct of surfaces that are amalgam	90%	•••	•••	•••	•••
Average amalgam surfaces / person	16.59	•••	18.00	40.00	• • •
Hg Waste (u+f) per amalgam surface ( $\mu$ g/d)	1.60	•••	1.58	1.64	•••
Human Hg waste $(u+f)$ in $\mu g/d$ [1]	26.54	•••	28.40	65.70	67.00
Convert to mg per year (multiply)	0.37	•••	0.37	0.37	• • •
Human Hg waste (u+f) in mg/yr	9.69	• • •	10.37	23.98	•••
Per Adult Person (including both those with and w/	out amalgams)				
Pct. Of population w/ fillings	65%	•••	75%	75%	65%
Overall avg. amalgam surfaces / person	10.78	7.60	13.50	30.00	•••
Hg Waste $(u+f)$ per amalgam surface $(ug/d)$	1.60	1.50	1.58	1.64	•••
Overall avg. human waste $(u+f)$ in $ug/d/pers$	17.25	11.44	21.30	49.28	•••
Convert to mg per year (multiply)	0.37	0.37	0.37	0.37	•••
Overall avg. human waste (u+f) in mg/yr/pers	6.30	4.17	7.77	17.99	•••
Notes.					pretation by
[1] Equation: Hg $(u+f) = c + m * N$				Bar	ron (2001b)
с	0.00	(Hg = 0  when  Am)	algam surfaces = 0		
m	1.60	(Hg Waste per am	algam surface)		
Ν	16.59	(No. of surfaces)	- /		
Hg (u+f) µg/d	26.54	u = urine wastes;	f = fecal wastes		

#### **Table 7. Human Waste Mercury Calculations**

Skare data and curve fit include a person with 82 surfaces. The lower end of Skare's data seems more applicable to the US & Canada.

[2] Interpretation of Skare ("low" = 18 surfaces, "mid" = 40 surfaces)

[3] Interpretation of O'Connor

Caution: Four digits used to show arithmetic, not to imply accuracy.

#### Load Calculation

The first step in assessing the contribution of pollution prevention to effluent reduction was to estimate the quantity of mercury in treatment plant influent that is contributed from the identified sources. The following business categories and residential activities were determined to be potentially significant sources and were, therefore, included in the influent load calculation.

#### **Commercial Activities**

- Dental offices
- Hospitals
- Laboratories
- Universities

#### **Residential Sources**

- Human waste (amalgam)
- Human waste (dietary)
- Laundry graywater

- Secondary schools
- Medical clinics
- Vehicle service facilities
- Industrial activities
- Household products
- Improper disposal of mercury thermometers

#### **Other Sources**

- Industrial activity
- Stormwater inflow

To estimate the load from each of the business categories for a given community, the number of businesses in a category (provided by the case study POTW) was multiplied by an average flow and mercury concentration for this business category. The average flow and concentration values were compiled from the literature and from data provided by agencies that have conducted this type of sampling. Loadings from residential activities were estimated on a per person or per household basis also based on literature values and multiplied by the service area population or number of households (provided by the case study POTW). It was assumed that commercial and residential activities do not vary from community to community allowing pooling of available data and application of these data to each of the case study participant. Equations used to estimate source loadings are shown in Table 11. Total influent loading was then determined as the sum of the loadings calculated for the individual residential, commercial, and industrial sources. Stormwater inflow and septage waste were estimated to be small contributions but were considered if the agency provided specific data.

#### **Reduction Estimate**

The next step in the process was to identify source control strategies for the sources listed above and to assign an effectiveness rating to each strategy. The predicted effectiveness of a control strategy was then multiplied by the estimated load for each applicable source to estimate a potential reduction achievable in the source's loading through pollution prevention. The procedure for predicting effectiveness and estimating reductions is described below. The effectiveness of a source control strategy can be estimated on the basis of the level of

participation expected and the maximum load reduction that may be achieved by the strategy. This is determined as the product of a participation factor and a load factor.

The participation factor is an estimate of the portion of the targeted audience that will make the desired behavior change and implement the recommended practice. Ideally, implementation of a control strategy would result in the elimination of the source it was designed to address. In reality, only a certain percentage of the people and procedures addressed by the strategy will change. Pollution prevention programs typically rely on voluntary actions. In the case of residential sources, agencies do not have the legal authority to regulate residents so, in general, voluntary approaches are the only strategies available. There are other strategies that may seem useful for residential sources such as product bans or changing building codes. These strategies are often outside the jurisdiction of the local POTW. To pursue these strategies, efforts must be coordinated regionally or at the state level. In some cases, agencies have worked together and with state legislators to achieve product bans or restrictions (e.g., San Francisco Bay Area restrictions on the use of copper sulfate root control products, California ban on lindanecontaining head lice remedies, statewide bans on mercury fever thermometers). In other situations, the agency that the POTW must work with that has the authority to achieve the desired change is less cooperative. For example, in California, there is an ongoing and, so far, unsuccessful effort to change the state plumbing codes to allow the use of non-copper plumbing materials. Therefore, available approaches for residential sources are primarily voluntary and outreach-based. Product bans and other approaches requiring support by other groups are more difficult to accomplish and require longer time periods and greater resources than public education. Therefore, participation rates used in this study for strategies requiring cooperation with other agencies are typically lower than public education.

For commercial sources, voluntary programs can be effective and may be more cost effective for the agency than working with the general public. Regulatory approaches are also available for commercial sources and will have higher participation rates than voluntary approaches during the initial stages of a program. Over time, an effective voluntary program can achieve participation rates comparable to regulatory programs. Specific participation rates used for this study are listed below. The participation rate used for dentists with respect to implementing BMPs on a voluntary basis is based on the results of surveys conducted regarding dental office waste management practices in San Francisco. San Francisco and other Bay Area agencies have worked with the dentists in its service area for a number of years educating them regarding the environmental impacts of mercury and recommended amalgam management practices. San Francisco Bay area dentists have been responding reasonably to data that is presented to them indicating that they are a major source of mercury in wastewater. The California Dental Association has been cooperating in recommending non-treatment related BMPs. However, their acceptance of separators remains to be seen. Surveys (231 responses from a possible 843 dentists) and site visits (34 offices) conducted for San Francisco dentists both indicate that approximately 65% of the dentists are implementing the recommended BMPs (WERF, 2001). WLSSD has also worked closely with the dental community and, after 10 years, reports high rates of cooperation from the dentists (Tuominem, 2001). However, participation rates can vary. King County reported a lower BMP implementation rate of 38% (King County, 2000).

The loading factor is the expected amount of pollutant load reduction from a source if there was 100% participation. The loading factor varies depending on the sources that the strategy addresses. Loading factors are determined by estimating the amount of mercury coming from individual sources within a category and determining what portion of the loading is addressed. For example, sources of mercury from hospitals include mercury-containing equipment, mercury solutions and mercury present in the sewer lines. Each control strategy is then examined to determine the individual sources that it addresses.

Business outreach and public education strategies are assumed to address all individual sources. For example, all programs related to thermometers and contact lens solutions have a loading factor of 100% because control strategies aimed at these sources would effectively eliminate the source. In the case of dentists, it was determined that approximately 80% of the dental amalgam wastes would be kept out of the drain because that is the approximate amount of material captured in standard traps. The load factor for amalgam separators is 95% because they are able to capture smaller particles and, therefore, a larger percentage of the amalgam wastes discharged. The load factor for stopping use of amalgam is 50% because it is estimated that about half the amalgam discharges in a practice come from placing fillings. The other half comes from removal of old amalgam fillings. This division between fillings placed and fillings removed is based on the responses of dentists surveyed in the San Francisco Bay Area (WERF, 2001).

The strategies available for addressing the identified sources and their predicted effectiveness are shown in Table 8. The participation and load factors are based on the results observed from various pollution prevention efforts. Some specifics include:

- The participation rate of 65% for the strategy targeting dental offices of voluntary implementation of BMPs is based on the results of surveys conducted in 2000 by Palo Alto, San Francisco, and Central Contra Costa Sanitary District (WERF, 2001; Brandenburg, 2000; Hughes, 2000).
- The load factor is based on the percent capture of amalgam particles through chair-side traps and vacuum filters estimated by MWRA and MCES studies (MWRA, 1997; WEF, 1999).
- The load factor for amalgam separators is based on the results of performance tests on separators. The participation factor associated with persuading dentists to stop using amalgam is based on the dental survey results mentioned above (WERF, 2001).
- The participation factor for the other business categories is based on percent of businesses complying with BMPs seen by Palo Alto and West County in the first year of voluntary programs conducted by these agencies for vehicle service facilities and is approximately 50% (WERF, 2000).
- The load factor for all the businesses that had BMP/modified purchasing are based on reductions measured by Detroit [Williams, 1997] and MWRA [MWRA/MASCO, 1995] for hospitals implementing these practices. For hospitals going to 'Mercury-Free' operation, the reductions may be greater than those observed in Detroit and Massachusetts. However, the reduction may not be 100% if there is residual mercury deposits in the laterals. In the

absence of other data, the load factor is based on the results measured in these two studies (i.e., 60%).

- The vehicle service load factor is based on West County monitoring results for its vehicle service program (WERF, 2000).
- The thermometer exchange program participation rate is based on results of programs conducted by San Francisco, Palo Alto, and Connecticut. For each of these programs approximately 1% of the service area population turned in thermometers.
- A review of several surveys assessing increased awareness or behavior change resulting from public education programs was used to set participation rates for residential source control strategies. Residential participation rates (i.e., reported behavior change) are typically 5-10% with much lower participation seen for a more complicated strategy (like removing amalgam fillings or installing a graywater system).
- Research regarding graywater systems has indicated that this is a complicated strategy for homeowners to implement. In some cases, it is not even possible due to space limitations. Graywater systems divert the water to landscaping and in densely populated areas not enough landscaping is available to accommodate the graywater discharges. Therefore, a lower participation rate is used (i.e., 2%).
- All participation rates used are the participation observed in the initial stages of a program, typically the first year. In this sort of time frame, regulatory approaches will have higher participation rates than voluntary programs. However, over time, participation rates for well-implemented voluntary programs will approach the participation rates for regulatory programs. After ten years, WLSSD has a high level of cooperation with the dentists in its service area (i.e., close to 100%). Palo Alto's vehicle service program had a 50% participation rate in its first year. After 5 years, participation and BMP implementation was over 90% (WERF 2000).

Source	Control Strategy	Participation Factor	Load Factor	Effectiveness
COMMERCIAL				
	Voluntary programs			
	BMPs - Recycle all amalgam wastes	65%	80%	52%
	Amalgam separators	10%	95%	10%
Dantista	Stop using amalgam	25%	50%	13%
Denusts	Permits/regulatory			
	BMPs - Recycle all amalgam wastes	95%	80%	76%
	Amalgam separators	90%	95%	86%
	Stop using amalgam	90%	50%	45%
Hospitals Laboratories Universities Secondary Schools Medical Clinics	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%
Vehicle Service	BMPs / Zero discharge	50%	80%	40%
Pottery Ceramics	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%
RESIDENTIAL				
Human Waste- amalgam	Remove amalgam fillings – public outreach	2%	100%	2%
Human Waste- dietary	Uncontrollable			
Laundry Graywater	Graywater systems- public outreach	2%	100%	2%
Household products	Substitute alternatives-public outreach	10%	100%	10%
	Turn in Hg thermometers - public outreach	1%	100%	1%
Thermometers	Work w/ pharmacies to not sell	50%	100%	50%
	Local sales ban	90%	100%	90%
Contact Lens Solution	Work w/ pharmacies to not sell	50%	100%	50%
	Local sales ban	90%	100%	90%
INDUSTRIAL	BMPs	90%	90%	81%

 Table 8. Source Control Strategies and Their Respective Effectiveness

#### Resulting Influent, Effluent and Biosolids Loads and Concentrations

Source reduction estimates were made for each identified source of mercury. These reduction estimates were then added together to estimate an overall influent reduction. Reductions were calculated based on two types of programs, pollution prevention/voluntary and source control/regulatory. A pollution prevention program was an all voluntary program and was based on implementation of the top three commercial and top two residential voluntary strategies with respect to estimated achievable reduction. A source control program included regulatory elements for the largest sources (i.e., dentists) and was calculated by assuming implementation of all reduction strategies. These estimates were tailored to each plant based on existing pollution prevention efforts as some plants had already implemented many of the strategies listed in Table 8 and other plants were just beginning their source control and pollution prevention programs.

Once a reduced influent concentration was established for each plant, reduced effluent concentrations could be calculated. Effluent reduction was determined using average removal efficiency calculated from influent and effluent data provided by each plant [(average influent – average effluent)/ average influent]. The range of removal efficiencies from plant to plant was 96% - 99%. Another approach to determining removal efficiencies was to consider any correlation between influent concentration and removal efficiency. It has been found that there may not be a linear correlation between influent and effluent concentration. Data provided by Western Lake Superior Sanitary District (WLSSD) and Sacramento Regional County Sanitation District (SRCSD) is shown in Figures 2 and 3. These figures indicate that as influent mercury concentration decreases, removal efficiency might also decrease. However, because of the variability of the data, no systematic approach for determining how much the removal efficiency decreases with decreasing influent could be established. Therefore, the average removal efficiency for each treatment plant was used as a best estimate.



Figure 2. SRCSD % Removal in Effluent vs. Influent Concentration



Figure 3. WL SSD% Removal in Effluent vs. Influent Concentration

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Biosolids reductions were determined based on the mass balance equation (influent – effluent = biosolids). Reduced influent and effluent values were used to calculate the reduction that plants would see in their biosolids concentrations. Reduced biosolids concentration is another beneficial effect of pollution prevention efforts.

#### Comparison to Effluent Limits

Mercury effluent levels, resulting from implementation of pollution prevention programs with the predicted effectiveness, were first determined using the process described above. The levels were then compared to water quality-based effluent limits. Table 9 lists criteria representing the range of limits that POTWs are facing.

Basis of Criteria	ng/L
Fish Tissue-based Criterion (Rivers/Streams)	17-18
Fish Tissue-based Criterion (Lakes)	7.5-7.8
Great Lakes Human Health Criterion	3.1
Great Lakes Initiative Wildlife Criterion	1.3
Proposed Maine Criterion	0.2

Table 9.	<b>Range of Mercury Criteria</b>
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Permits in the San Francisco Bay area have effluent limits based on the National Recommended Water Quality Criteria (12 ng/L). However, as these permits are reissued, the CTR criteria of 25 ng/L will be used. Agencies in the Great Lakes area have permit limits based on the Great Lakes Water Quality Initiative Criterion (1.3 ng/L) and, in Maine, 0.2 ng/L was under consideration.

In January 2001, EPA issued a water quality criterion for methyl-mercury defined as a level in fish tissue. Implementation of this criterion will be complicated as states struggle to use the fish tissue concentration in a regulatory context by attempting to convert the value into a water column number. EPA has set up a workgroup to develop implementation guidance for the criterion and water-quality standards based on it. This guidance could result in changes in the way POTW compliance is defined. For the purposes of this study, water quality criteria calculated from the fish tissue criterion were considered by using default values to translate the fish tissue criterion to a water quality criteria. The calculated values are shown in Table 9. The actual values of water quality criteria developed from the fish tissue criterion will depend on the specific water body and its properties.

The calculated effluent concentrations (based on applying estimated reductions to maximum observed and average effluent concentrations reported by the POTWs) were then compared to the range of criteria in Table 9. Compliance with criteria was determined 'end-of-pipe' (i.e., no dilution). Permits containing mercury effluent limits are often applied with no credit for dilution. This is either because the receiving water is impaired for mercury (303(d) listed) or because the receiving water is an effluent dominated water body.

### Cost of Compliance

The cost to comply with the criteria in Table 9 was determined based on the costs to implement the proposed pollution prevention programs and, as necessary, to construct additional treatment facilities where reductions through pollution prevention were inadequate. The costs to businesses targeted by pollution prevention programs was not considered. However, if treatment is required of dentists there would be a cost to install amalgam separators (\$100 to \$3000 installed) and to maintain the system (\$35 - \$200/month) [Barron, 2001; Boyd, 2001].

Pollution prevention costs were estimated based on a review of the cost of effective pollution prevention programs and the cost to develop demonstration pollution prevention projects [LWA, 2001; WERF, 2000]. The costs of several pollution prevention program elements are shown in Table 12. In general it was assumed that a pollution prevention/voluntary program would address dentists, two other business categories and a public education campaign. The program would be conducted on a voluntary basis and would roughly cost the following (based on the costs of pollution prevention programs shown in the Table 12):

- Program for dentists, voluntary \$100,000
- Voluntary BMP based program for other businesses \$50,000
- Public education program \$50,000 for agencies <20 MGD; \$100,000 for agencies between 20 and 100 MGD; \$150,000 for agencies >100 MGD

The cost associated with a source control/regulatory program factors in costs of each strategy listed. In addition, costs for implementing a program with regulatory elements were considered. Implementing a regulatory or permit-based program is more costly than a voluntary program in that it requires more tracking and paperwork to assess compliance. However, permit based programs for small dischargers (e.g., dentists) do not have to be as resource intensive as standard pretreatment permits. Agencies have implemented general or group permits for small dischargers (e.g., photoprocessors) or have developed permits that have fewer requirements or are BMP-based. It was assumed that a regulatory program for dentists would be twice as costly as a voluntary program and, therefore, would have an annual cost of \$200,000.

Treatment costs were determined based on a study conducted by the Sanitation Districts of Los Angeles County (LACSD) for the unit operations directly associated with mercury removal (i.e., reverse osmosis and ion exchange). Waste removal costs were estimated by ADVENT. This results in an annual treatment cost of \$1,922,000/ MGD as shown in Table 10.

Table 10. Annual Treatment Costs for Kentoving Mercury					
Unit Process	Total Cost (\$ 10 <sup>3</sup> /MGD)	Reference Source			
Reverse Osmosis	876	National Research Council			
Ion Exchange	900	Bureau of Reclamation <sup>3</sup>			
Brine treatment	146	ADVENT			
Total	1922				

 Table 10. Annual Treatment Costs for Removing Mercury<sup>2</sup>

These costs were applied to a portion of the total plant flow based on the reduction needed to meet proposed limits after the reductions achieved through pollution prevention were considered. The amount of flow treated was estimated as shown in Table 11.

Reduction needed	Portion of flow treated	Annual cost multiplied by
>75%	100%	100%
50%-75%	75%	75%
25%-50%	50%	50%
0%-25%	25%	25%

#### Table 11. Cost Based on Reduction Needed

<sup>&</sup>lt;sup>2</sup> Includes amortized capital and operation and maintenance costs.

<sup>&</sup>lt;sup>3</sup> *Mercury and Cadmium Fact Sheet*, Bureau of Reclamation, Technical Service Center, Denver, CO, September 1999.

Source	P2 Item	Number in Target Audience	Annual/ Start-up Cost	Source
Dentists	Brochure/ Fact Sheets + distribution	900	\$60,000	SFWPPP
	Brochure/ Fact Sheets + distribution	500	\$12,000	Palo Alto RWQCP
	Outreach/advisory group	500 dentists	\$10,000	Palo Alto RWQCP
	Outreach	100	\$30,000	WLSSD
	Site visits	35 visits	\$12,000	SFWPPP
Consumer Products	Thermometer exchange program	3.3 million people, 38,000 thermometers	\$144,816	Connecticut DEP
	Thermometer exchange program	790,000 people, 5000 thermometers collected	\$70,000	SFWPPP
	Thermometer exchange program	227,000 people, 1000 thermometers	\$15,000	Palo Alto RWQCP (KM)
	Thermometer Sales ban/ legislation		\$15,000	Palo Alto RWQCP
	Root killer sales ban legislation		\$30,000	Palo Alto RWQCP (KM)
	HHW Collection facility/event	76 collection events	\$ 2,660	Connecticut DEP
Vehicle Service	Site visits/inspections	330 facilities	\$20,000	Palo Alto RWQCP (KM)
	Develop permits	330 facilities	\$50,000	Palo Alto RWQCP (KM)
	Inspections/BMPs	46 facilities	\$50,000	West County
Secondary Schools	Clean-out/ collection of chemicals	8 high schools	\$40,000	Connecticut DEP
Non-Hg Sources	Brochure development & printing	50,000 people, 6000 guides	\$12,000	Davis healthy gardens
	General public outreach	50,000 people	\$40,000	Davis healthy gardens
	Residential outreach	20,000 residents, 1000 packets	\$12,000	Woodland O&G
	Business outreach/ recognition program	200 businesses	\$20,000	Davis Partners Program
	8 fact sheets/ BMPs, regulatory info	500 businesses	\$20,000	Davis Partners Program
	Business workshops (2)	1000 businesses	\$27,000	Santa Monica New Development Program
	Brochure/ fact sheets -general		\$15-20,000	General depending on size, number, etc.
	Clean Bay Hardware program		\$20,000	Palo Alto RWQCP (KM)

 Table 12. Costs of Pollution Prevention Programs

## **Results and Discussion**

The results of the analysis are discussed below in the following sections:

- Select Case Studies
- Calculate Load Estimates
- Identify Most Significant Sources
- Estimate Influent Reductions
- Determine Resulting Effluent Concentrations
- Assess Potential Compliance
- Estimate Changes in Biosolids Levels

- Determine Costs Associated with Compliance
- Assess Impact of Assumptions

#### Select Case Studies

A large quantity of quality information was received from a number POTWs throughout the mercury source control study. However, for the final report, only a few of these agencies were examined more closely. The selection of these final plants was based on four criteria as listed in the Procedure section. First, the quantity of data available for each plant's influent, effluent and biosolids was evaluated. As shown in Table 2, Portland Water District's Portland plant had only one influent sample and with the variability of influent mercury sampling, it was decided not to use Portland for the final calculations. Second, the analytical method used and subsequent detection limit were investigated. As shown in Table 2, Green Bay Municipal Sanitation District (GBMSD), the Massachusetts Water Resources Authority (MWRA) and Western Lake Superior Sanitation District (WLSSD) presently use EPA Method 245.1 for mercury analysis. This method has a higher detection limit than EPA Method 1631 and, due to the variance this causes in influent and effluent concentrations, it is not appropriate to compare plants that use Method 245.1 to those using Method 1631. Only plants using EPA Method 1631 were included in the final calculations with the exception of WLSSD because they use an improved method of 245.1 that has a lower detection limit of 5 ng/L. The third criterion involved a comparison of influent to effluent plus biosolids. Calculating this mass balance was useful for evaluating the consistency of the collected data. Comparisons between influent and effluent plus biosolids were used to identify plants with acceptable mass balance closure. The measured influent load is the product of average flow and average concentration. In addition, "Effluent + Biosolids" was calculated to provide another measure of influent load. The measured influent and effluent plus biosolids loads for each plant are compared in Table 13.
DOTW		Community	grams Hg / day					
POTW		Size	Effluent	Biosolids	Effluent + Biosolids	Influent		
MWRA	MA	2.5 M	42.6	340	383	369		
HRSD	VA	1.5 M	0.7	1.37	2.07	110		
SRCSD	CA	1.1 M	5.44	113	118	135		
NEORSD - Easterly	OH	401,167	1.4	55	56.4	56.3		
NEORSD - Southerly	OH	597,936	1.3	124	125.3	134		
NEORSD - Westerly	OH	123,170	0.36	16	16.4	13.3		
San Francisco - SE	CA	564,744	5.2	< 0.323*	5.4	101		
San Francisco - OS	CA	224,033	3.4	<0.097*	3.4	15.8		
WLSSD	MN	95,000	0.69	16.3	17	15		
Palo Alto	CA	226,000	0.555	25.2	26.1	23.2		
GBMSD	WI	180,900	0.73	18.9	19.6	10.8		
Portland	ME	60,000	0.869	8.47	9.34	6.27		
LAWPCA	ME	50,000	0.23	10.15	10.38	3.23		
Novato	CA	34,190	0.38	?	?	8.61		
Westbrook	ME	15,000	0.066	1.51	1.58	2.67		

**Table 13. POTW Mass Balances** 

\* 1/2 MDL was used in effluent + biosolids calculation

Box plots were created to show the distribution of influent data as well as effluent plus biosolids data. If the influent (i) and effluent + biosolids (e+b) boxes overlapped, the range of influent values was considered statistically equivalent to the effluent plus biosolids values. Based on the comparison shown in Figure 4, Portland Water District's Portland plant was removed from the list, as well as Lewiston-Auburn Water Pollution Control Agency (LAWPCA) and GBMSD. San Francisco's biosolids data was non-detect for 2000 and therefore did meet the mass balance criteria.



#### **Figure 4. Box Plots of Influent and Effluent + Biosolids**

The final criterion evaluated to select the case studies was the availability of all requested information. It was not possible to obtain enough data from Hampton Roads Sanitation District (HRSD) or Novato Sanitation District to make key calculations, therefore they were not included in the final assessment.

Therefore, the plants used as case studies were:

- Northeast Ohio Regional Sewer District, Ohio Easterly Plant (NEORSD-e)
- Northeast Ohio Regional Sewer District, Ohio Southerly Plant (NEORSD-s)
- Northeast Ohio Regional Sewer District, Ohio Westerly Plant (NEORSD-w)
- Palo Alto Regional Water Quality Control Plant, California (Palo Alto)
- Sacramento Regional County Sanitation District, California (SRCSD)
- Portland Water District, Maine Westbrook Plant (Westbrook)
- Western Lake Superior Sanitary District, Minnesota (WLSSD)

### Calculate Load Estimates

Once the case study plants were selected, the next step was to calculate an influent load from the individual source loading contributions. Source loading contributions were determined using the procedure discussed above and the values listed in Appendix B. The estimated influent load for each plant was computed as the sum of the estimated mercury loads from each source. Percent closure estimates were obtained by using the estimated influent concentration as well as the measured effluent and biosolids concentrations and are presented in Table 14. The calculated influent load accounts for a large percentage of the measured influent load, the worst case being SRCSD, where 30% of its influent mercury is unaccounted for. A sample load calculation for one agency is shown in Table 15.

POTW	Flow (mgd)	Estimated Influent Load (g/d)	Measured Influent Load (g/d)	Effluent + Biosolids (g/d)	% closure (Estimated/ Measured)	% closure (Effluent+Biosolids/ Measured)
NEORSD - e	104.1	40.9	56.3	56.4	73%	100%
NEORSD - s	109.5	117.5	133	125	88%	94%
NEORSD - w	31.1	13.1	13.3	16.4	98%	123%
Palo Alto	28	20.1	23.2	25.8	87%	111%
SRCSD	157	88.2	135	118	65%	88%
Westbrook	2.51	2.4	2.7	1.58	90%	58%
WLSSD	39	11.7	15.6	17.0	75%	109%

Table 14. Closure of Measured and Estimated Influent Loads

The estimated mercury loadings were grouped into residential, commercial and industrial contributions as shown in Figure 5. Commercial sources represent the largest percentage of the influent loading, due largely to dental wastewater discharges. As shown in Figure 5, industrial mercury loads represent a relatively small portion of the total influent load.



Figure 5. Estimated Load Closure

14			mpre or E			0111 10		
Source	#	Conc	Units	Flow/ Facility	Units	Load	Units	Calculation
Commercial								
Dentists	500	0.056	g/dentist/day			28.00	gm/day	Number of dentists x concentration
Medical Clinics	80	4.3	μg/l	2800	gal/day	3.65	gm/day	Number of medical clinics x flowx concentration
Hospitals	39	4.39	μg/l	120000	gal/day	77.76	gm/day	Number of hospitals x flow x concentration
Laboratories	77	0.37	μg/l	11000	gal/day	1.19	gm/day	flow x concentration x number
Universities		0.17	μg/1	48500	gal/day	0.00	gm/day	flow x concentration x number
Secondary Schools		0.3	μg/l	7000	gal/day	0.00	gm/day	flow x concentration x number
Vehicle Service	1284	1.2	μg/l	500	gal/day	2.92	gm/day	flow x concentration x number
Pottery/ Ceramics Studios	200	0.31	μg/l	168	gal/day	0.04	gm/day	number x flow x concentration
Estimated Commercial Load						113.55	gm/day	
Residential								
Population	1100000			100	gal/person/da y			
Number of Households	326000			168	gal/house/ day			
Human Waste (amalgam)		17.2	µg/person/day			12.30	gm/day	population x concentration x 65% population w/ fillings
Human Waste (dietary)		1.4	µg/person/day			1.54	gm/day	population x concentration
Laundry Graywater		8.4	µg/person/day			9.24	gm/day	population x concentraiton (1 load per person per week)
Household Products		0.021	µg/house/day	1.10E+08	gal/day	8.74	gm/day	residential flow x concentration
Thermometers		2.3	µg/house/day			0.75	gm/day	number of households x 22µg/house/day x 52% of households own hg therm.
Contact Lens Solution		0.044	µg/person/day			0.05	gm/day	popluation x concentration
Estimated Residential Load						32.62	gm/day	
Industrial		0.21	μg/l	8570000	gal/day	6.81	gm/day	
Estimated Influent						152.98	gm/day	
Measured Influent		0.199	µg/l	1.57E+08	gal/day	118.25	gm/day	

 Table 15. Example of Load Estimation from Identified Sources

# Identify Most Significant Sources

The next step was to determine the sources that accounted for the greatest contributions to the influent loading. For the seven plants examined in this study, dentists, hospitals, medical clinics and vehicle service facilities represented the largest commercial mercury sources for each agency. Figure 6 shows the rankings for these top four commercial mercury sources. As the "First" rank exhibits, in all seven plants, dentists are the greatest contributors to the mercury load. The next greatest loading, or "Second" rank, comes from mainly hospitals (6 of 7 plants).

Finally, the third greatest contribution to mercury loading comes from medical clinics for most of the plants, with vehicle service facilities and hospitals also contributing.





Based on average source contributions identified for each POTW, the largest residential source was human waste due to amalgam fillings for all seven plants. Laundry graywater and household products were the second and third largest sources respectively for all seven plants.

The relative contributions of each of the identified mercury sources are shown in Figure 7. The values shown in Figure 7 are the average percent contributions for the source for all seven plants. Dentists are the largest source by far when compared to average contributions from the other sources. Human waste amalgam and hospitals are the next most significant sources.



Figure 7. Average Source Contributions to Influent Mercury Load

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### Estimate Influent Reduction

The estimated reduction achievable through pollution prevention was then determined for each plant. Load reductions were calculated using a participation factor, load factor and effectiveness for each identified control strategy as described in the Procedure section above. An example of the reduction estimate calculated for one plant is shown in Table 16.

	Estimated		Participation	Load	Effective-	Load
Source	Load (gm/day)	Control strategy	Factor	Factor	ness	Reduction
Commercial						
		Voluntary programs				
	1.4	BMPs - Recycle all amalgam wastes	65%	80%	52%	0.7280
	1.4	Amalgam separators	10%	95%	10%	0.1330
Dentists	1.4	Stop using amalgam	25%	50%	13%	0.1750
Dentists		Permits/regulatory				
	1.4	BMPs - Recycle all amalgam wastes	95%	80%	76%	1.0640
	1.4	Amalgam separators	90%	95%	86%	1.1970
	1.4	Stop using amalgam	90%	50%	45%	0.6300
Hospitals	0.3323	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%	0.0997
Laboratories	0.0154	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%	0.0046
Universities	0.0000	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%	0.0000
Secondary Schools	0.0477	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%	0.0143
Medical Clinics	0.0911	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%	0.0273
Vehicle Service	0.0545	BMPs / Zero discharge	50%	80%	40%	0.0218
Pottery Ceramics	0.0004	BMPs -Modify purchasing/ disposal practices (voluntary)	50%	60%	30%	0.0001
Commercial Total	1.9414		•		•	
Residential						
Human Waste-amalgam	0.1677	Remove amalgam fillings	2%	100%	2%	0.0034
Human Waste-dietary	0.0210	uncontrollable				0.0000
Laundry Graywater	0.1260	graywater systems	2%	100%	2%	0.0025
Household products	0.1192	Substitute alternatatives	10%	100%	10%	0.0119
	0.1192	HHW collection	13%	100%	13%	0.0155
Thermometers	0.0112	Turn in Hg thermometers - low	1%	100%	1%	0.0001
	0.0112	Work w/ pharmacies to not sell	50%	100%	50%	0.0056
	0.0112	local sales ban	90%	100%	90%	0.0100
Contact Long Solution	0.0007	Work w/ phormacies to not call	90% 50%	100%	50%	0.0100
	0.0007		000/	100%	00%	0.0005
Destined 177 (1	0.0007	iocai sales ban	90%	100%	90%	0.0006
Residential Total	0.4457	<b>BMD</b> <sub>2</sub>	000/	000/	<b>Q10</b> /	0.0200
Total Estimated Local	0.0480	DIVITS	90%	9U%	01%	1 4202
Total Esumated Load	2.4352			N		1.4203
Average Influent Load	1.5771			Realis	tic Reduction	0.9065

Table 16.	Source	Reduction	Estimation	Example
1 anic 10.	bource	<b>M</b> Cuuchon	Lounation	Блатріс

Using this table it was possible to develop two reduction estimates, one for pollution prevention/ voluntary programs and another for source control (semi-regulatory) programs, as discussed previously. The pollution prevention (voluntary) reduction estimates included reduction strategies for the top three residential sources, top two commercial sources, and industrial sources. Human waste is considered uncontrollable, except to the extent that less amalgam filling are placed by dentists. For commercial sources, dentists were the major commercial contributors to the influent load for every agency. The pollution prevention (voluntary) reduction strategy used for dentists was to encourage BMPs or require amalgam separators for agencies that had tried BMPs. The source control method of estimating mercury reduction assumes that control strategies are implemented for all commercial, residential and industrial sources and that dentists have a regulatory program. The subsequent pollution prevention and source control percent reductions for each agency can be found in Table 17. The average pollution prevention reduction is 26% while the average source control reduction is 37%.

POTW	Flow (mgd)	Measured Influent Load (g/d)	% Reduction <b>Pollution</b> <b>Prevention</b>	% Reduction Source Control
NEORSD - e	104.1	56.3	24%	39%
NEORSD - s	109.5	133	20%	29%
NEORSD - w	31.1	13.3	29%	44%
Palo Alto	28	23.2	14%	14%
SRCSD	157	135	23%	32%
Westbrook	2.51	2.7	58%	90%
WLSSD	39	15.6	12%	12%

 Table 17. Pollution Prevention and Source Control Reduction

The estimated reductions for Palo Alto and WLSSD are low because these agencies have mature pollution prevention programs and have implemented many of the strategies listed in Table 12. Therefore, few additional reduction opportunities exist in their service areas.

### Estimate Resulting Effluent Concentrations

After estimating the reduction of mercury in each plant's influent, resulting effluent concentrations were calculated using each plant's average reported removal efficiency. As mentioned previously, this is an optimistic assumption because as influent concentrations get lower it is likely that removal efficiencies decrease as well. Tables 18 and 19 report the reduced influent and effluent concentrations for the pollution prevention and source control programs, respectively. They also provide a comparison of the reduced effluent concentrations ("*Pollution Prevention/Source Control Reduced Ave. Effluent*") to the effluent concentrations prior to source control ("*Ave. Unreduced Effluent*").

POTW	Flow (mgd)	Ave. Measured Effluent + Biosolids (ppt)	Pollution Prevention Reduced Influent (ppt)	Ave. Plant Removal Efficiency	Pollution Prevention Reduced Ave. Effluent (ppt)	Ave. Unreduced Effluent (ppt)
NEORSD - e	104.1	143	108	97%	3.25	3.56
NEORSD - s	109.5	302	209	99%	2.09	3.17
NEORSD - w	31.1	139	98.1	97%	2.94	3.11
Palo Alto	28	246	212	97%	5.32	5.50
SRCSD	157	199	154	96%	6.17	9.00
Westbrook	2.51	166	70.4	98%	1.41	6.90
WLSSD	39	115	102	96%	4.07	4.70

 Table 18. Resulting Concentrations Using Pollution Prevention/Voluntary Estimates

 Table 19. Resulting Concentrations Using Source Control/Regulatory Estimates

POTW	Flow (mgd)	Ave. Measured Effluent + Biosolids (ppt)	Source Control Reduced Influent (ppt)	Ave. Plant Removal Efficiency	Source Control Reduced Ave. Effluent (ppt)	Ave. Unreduced Effluent (ppt)
NEORSD - e	104.1	143	87.8	97%	2.63	3.56
NEORSD - s	109.5	302	162	99%	1.62	3.17
NEORSD - w	31.1	139	78.5	97%	2.35	3.11
Palo Alto	28	246	211	97%	5.29	5.50
SRCSD	157	199	135	96%	5.39	9.00
Westbrook	2.51	166	16.3	98%	0.33	6.90
WLSSD	39	115	102	96%	4.06	4.70

# Assess Potential Compliance

Using the reduced effluent concentrations it was possible to compare the new, reduced concentrations to the range of mercury criteria. Tables 20 and 21 list the number of plants (out of 7) that meet the mercury criteria based on no pollution prevention, pollution prevention/voluntary and source control/regulatory. Using average effluent concentrations, all agencies meet the 18 ppt criteria (and the 50% margin of error value, 9 ppt; see below for discussion) before any pollution prevention or source control is implemented. Pollution prevention and source control help one agency meet the 7.8 ppt criteria. None of the agencies are able to meet the 0.2 ppt criteria with pollution prevention or source control alone. Basing compliance on reductions achieved compared to maximum effluent concentrations for each plant, only 4 plants have maximum effluent levels prior to source control nelps two agencies comply with the 18 ppt criteria. Both programs help two agencies comply with the 7.8 ppt criteria. No agencies are able to meet the 1.3 ppt or 0.2 ppt criteria when maximum effluent concentrations for each plant, only 4 plants have maximum effluent levels prior to source control helps two agencies comply with the 18 ppt criteria. Both programs help two agencies comply with the 7.8 ppt criteria. No agencies are able to meet the 1.3 ppt or 0.2 ppt criteria when maximum effluent concentrations are considered.

Some of the reduced effluent concentrations are very close to the criteria used for evaluation as shown in Tables 20 and 21. It is important to recognize that plants do not operate to *just* meet criteria, there must be a safety factor. Effluent mercury levels resulting from reductions achieved through source control and pollution prevention are based on average values. Plants would be more likely to operate within a margin of safety to assure compliance. In some parts of the country, NPDES permit effluent limits are implemented as values never to be exceeded. Even one violation may result in stiff fines and other penalties. Therefore, plants designed to comply with these regulations are designed with margins of safety that will assure compliance at least 99.9% of the time (corresponding to an exceedance once in three years)(Tschobanoglous, 2001). A less extreme approximation of the need to operate with a margin of safety to assure compliance is to assume that a plant would operate with a 50% margin of safety. Therefore, in addition to the number of plants meeting a criteria by comparing effluent values directly to water quality criteria in Tables 20 and 21, effluent levels are compared to values set at half the criteria. The second column of each set shows the number of agencies meeting a mercury level set at half the criteria to account for a 50% margin of safety.

Table 20. Number of Agencies Meeting Criteria and 50% Factor of Safety Based on
Average Effluent Concentrations (Out of 7)

Criteria	18	9	7.8	3.9	1.3	0.65	0.2	0.1
Cilicila	ppt	ppt	ppt	ppt	ppt	ppt	ppt	ppt
No Program	7	7	6	3	0	0	0	0
Pollution Prevention	7	7	7	4	0	0	0	0
Source Control	7	7	7	4	1	1	0	0

# Table 21. Number of Agencies Meeting Criteria and 50% Factor of Safety Based onMaximum Effluent Concentrations (Out of 7)

Criteria	18	9	7.8	3.9	1.3	0.65	0.2	0.1
	ppt	ppt	ppt	ppt	ppt	ppt	ppt	ppt
No Program	4	2	2	0	0	0	0	0
Pollution Prevention	5	4	4	1	0	0	0	0
Source Control	6	4	4	2	0	0	0	0

### Estimate Changes in Biosolids Mercury Levels

The biosolids concentrations after pollution prevention or source control were calculated using the resulting influent and effluent concentrations (influent – effluent = biosolids). Table 22 shows the change in biosolids mercury levels from no pollution prevention to pollution prevention to source control. Pollution prevention and source control are able to reduce concentrations of mercury in biosolids by 11 - 90 %. It is possible that even more biosolids mercury reduction may be achieved as a result of pollution prevention and source control if the implemented practices reduce substantially the amount of particulate and solid materials

discharged. Since particulate mercury that reaches the plant influent is more likely to end up in the biosolids than in the effluent.

			-				
	Biosolids Concentration (grams/day)						
POTW	No D2	Pollution	Source				
	NO P2	Prevention	Control				
NEORSD - e	55.0	41.4	33.5				
NEORSD - s	124	85.6	66.5				
NEORSD - w	16.0	11.2	8.97				
Palo Alto	25.2	21.9	21.8				
SRCSD	113	87.9	76.8				
Westbrook	1.51	0.66	0.15				
WLSSD	16.3	14.4	14.4				

 Table 22. Estimated Biosolids Mercury Levels

### Determine Costs Associated with Compliance

The potential cost associated with compliance for each plant was determined as follows. The reduction needed to achieve an effluent level of 1.3 ppt was determined based on the maximum observed effluent concentration for each plant. The cost to achieve the estimated reduction was determined using the cost estimates for pollution prevention and source control programs described in the Procedure section. Any additional reduction needed to meet 1.3 ppt was assumed to be accomplished through additional treatment, the cost of which was estimated as described in the Procedure section. The resulting cost calculations are shown in Tables 23 and 24.

 Table 23. Pollution Prevention Using Maximum Effluent Concentrations for Cost

 Calculations

POTW	Ave. Op. Size (MGD)	Max Eff. (ppt)	Reduction to achieve 1.3 ppt	Reduction thru Pollution Prevention	Reduction thru Treatment after Pollution Prevention	Annual Pollution Prevention Cost (\$1000)	Tı Cos P Pr	Annual reatment st (\$1000) – With ollution revention	Tı Cos P Pr	Annual reatment st (\$1000) – No ollution revention
NEORSD-E	104.07	9.54	86%	24.3%	62.1%	\$350	\$	150,017	\$	200,023
NEORSD-S	109.49	5.84	78%	19.6%	58.1%	\$350	\$	157,830	\$	210,440
NEORSD-W	31.07	5.03	74%	29.4%	44.7%	\$300	\$	29,858	\$	44,787
Palo Alto	28	18.3	93%	13.8%	79.1%	\$250	\$	53,816	\$	53,816
SRCSD	157	24.9	95%	22.5%	72.2%	\$350	\$	226,316	\$	301,754
Westbrook	2.51	16.9	92%	57.5%	34.8%	\$250	\$	2,412	\$	4,824
WLSSD	39	29	96%	11.5%	84.0%	\$300	\$	74,958	\$	74,958

POTW	Ave. Op. Size (MGD)	Max Eff. (ppt)	Reduction to achieve 1.3 ppt	Reduction thru Source Control	Reduction thru Treatment after Source Control	Annual Source Control Cost (\$1000)	T Co - w	Annual reatment st (\$1000) ith Source Control	T Co	Annual reatment st (\$1000) - No P2
NEORSD-E	104.07	9.54	86%	38.6%	47.8%	\$700	\$	100,011	\$	200,023
NEORSD-S	109.49	5.84	78%	28.9%	48.9%	\$700	\$	105,220	\$	210,440
NEORSD-W	31.07	5.03	74%	43.5%	30.6%	\$600	\$	29,858	\$	44,787
Palo Alto	28	18.3	93%	14.3%	78.6%	\$300	\$	53,816	\$	53,816
SRCSD	157	24.9	95%	32.3%	62.4%	\$600	\$	226,316	\$	301,754
Westbrook	2.51	16.9	92%	90.1%	2.2%	\$550	\$	1,206	\$	4,824
WLSSD	39	29	96%	11.7%	83.9%	\$450	\$	74,958	\$	74,958

 Table 24. Source Control Using Maximum Effluent Concentrations for Cost Calculations

### Sensitivity Analysis

The impacts of the assumptions made in the above analysis were assessed in several ways. One approach was to vary the load values used for human waste and dental discharges to evaluate the impact of these numbers on the results. Subsequent sections provide details on the impacts of varying the school loading contribution and how a probability-based model was used to assess the impacts of the assumptions.

### Variation of Dental Discharge and Human Waste Values

The impact of the load values used for dental and human waste estimates was assessed as follows. Dental values were varied from 0.035 - 0.15 g/dentist/day to encompass the range of dental values found in the literature. Similarly, human waste values were varied from 11 - 43.6 µg/person/day. The cases examined are shown in Table 25.

Dental Discharge Estimate	Human Waste Amalgam Estimate
(g/dentist/day)	(µg /person/day)
0.056*	17.2*
0.035	11
0.035	43.6
0.15	11
0.15	43.6

 Table 25. Scenarios used to test dental and human waste assumptions

\*Base case

These values were carried through the reduction calculations to see the impact of using each of these scenarios on mass balance closure, influent reduction, effluent concentration, compliance and cost. Except for the mass balance closures, the values for human waste did not affect the calculation. Trends associated with varying these values were the same for the pollution prevention scenario and the source control scenario. Table 26 shows selected results for the pollution prevention scenario. More detailed results can be found in Appendix D.

Mass balance closures ranged from 96% to 192% when the high dental discharge number was used (i.e., 0.15 g/dentist/day). Using the 0.035/11 scenario resulted in low mass balance closures ranging from 56.5% to 77%. The mass balances that stayed closest to 100% closure were for the base case and the 0.035/43.6 scenario.

Estimated influent reductions ranged from a low of 7% to greater than 100% reduction. Reductions corresponded to the dental value used with much higher reductions seen when the 0.15 value was used. Reductions exceeding 100% were only seen when the high dental value was used. Similarly, variation in resulting influent and effluent concentrations also corresponded to the dental value used. In some cases, the use of the 0.15 g/dentist/day resulted in negative influent and effluent concentrations.

Compliance assessments were not impacted significantly by the scenarios. However, compliance did result slightly more often in the cases where 0.15 g/dentist/day was used as the assumed dental loading.

Treatment costs varied only slightly from case to case. The assumptions only had significant impact in those situations where no treatment was needed to achieve compliance. It should be noted that for 4 of the 6 situations where no treatment was necessary, the estimated effluent concentration was less than zero.

Figure 8 compares the average relative loadings from different sources for the different scenarios. Dentists were the largest source in every case, regardless of the loading values used. However, the percent of influent load attributed to dentists varied from approximately 25% to over 100%, depending on the value used for dentists. The final value used for this study resulted in dentists contributing on average 35% of the influent load. This seems plausible in that dentists are determined to be the main contributor to influent loading of mercury without the estimate being greater than 100% of influent mercury. Human waste contribution did not vary greatly between scenarios. Average contribution to influent loading ranged from 8 - 18%, depending on the value used for human waste loading. The final value used accounted for on average 13% of influent loading.

# Table 26. Results of Varying the Dental and Human Waste Values (g/dentist/day, µg /person/day)

	1 01001	n elesare (Ben	indice d / inie do di	<i>eu)</i>	
POTW	0.056, 17.2	0.035, 11	0.035, 43.6	0.15, 11	0.15, 43.6
NEORSD-e	73%	56.5%	71.6%	129%	145%
NEORSD-s	88%	70.3%	88.5%	158%	177%
NEORSD-w	98%	77.2%	97.0%	172%	192%
Palo Alto	87%	66.1%	93.0%	150%	177%
SRCSD	65%	54.2%	71.5%	96.8%	114%
Westbrook	90%	68.5%	80.3%	175%	187%
WLSSD	75%	58.8%	71.7%	132%	145%

Percent Closure (Estimated / Measured)

Table 26. (co	ont'd.)
---------------	---------

recent Reduction due to ronution revention/voluntary						
POTW	0.056, 17.2	0.035,	0.15,			
		11/45.0	11/45.0			
NEORSD-e	24%	17%	55%			
NEORSD-s	20%	15%	41%			
NEORSD-w	29%	22%	62%			
Palo Alto	14%	9%	34%			
SRCSD	23%	18%	43%			
Westbrook	58%	40%	135%			
WLSSD	12%	7%	30%			

Percent Reduction due to Pollution Prevention/Voluntary

Reduced Effluent Concentration due to Pollution Prevention/Voluntary (ppt)

POTW	0.056, 17.2	0.035, 11/43.6	0.15, 11/43.6
NEORSD-e	3.25	3.54	1.92
NEORSD-s	2.09	2.32	1.05
NEORSD-w	2.94	3.25	1.57
Palo Alto	5.32	5.61	4.06
SRCSD	6.17	6.53	4.52
Westbrook	1.41	1.98	-1.16
WLSSD	4.07	4.26	3.22

N	umber	of A	Agencies	Meeting	6 ppt	Criteria	Based	on A	Average I	Effluent

POTW	0.056, 17.2	0.035, 11/43.6	0.15, 11/43.6
Nothing	5	5	5
Pollution Prevention	6	6	7
Source Control	7	7	7

Number of Agencies Meeting 1.3 ppt Criteria Based on Average Effluent

POTW	0.056, 17.2	0.035, 11/43.6	0.15, 11/43.6
Nothing	0	0	0
Pollution Prevention	0	0	2
Source Control	1	1	4

Annual Treatment Costs With Pollution Prevention/Voluntary Maximum Effluent (\$1000)

POTW	0.056, 17.2	0.035, 11/43.6	0.15, 11/43.6
NEORSD-e	\$ 150,017	\$ 150,017	\$ 100,011
NEORSD-s	\$ 157,830	\$ 157,830	\$ 105,220
NEORSD-w	\$ 29,858	\$ 44,787	\$ 14,929
Palo Alto	\$ 53,816	\$ 53,816	\$ 40,362
SRCSD	\$ 226,316	\$ 226,316	\$ 0
Westbrook	\$ 2,412	\$ 4,824	\$ 3,618
WLSSD	\$ 74,958	\$ 74,958	\$ 56,219



Figure 8. Average Relative Contributions of Mercury Sources (g/dentist/day, µg /person/day)

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### Influence of Secondary School Values

It has been suggested that secondary schools may release as much mercury as hospitals, even though the limited data available for this study showed schools to release approximately 0.3 g/day to the sewers. Increasing the value used for schools in the loading calculations to be the same as the hospital value (4.39 g/day) produced an average change in secondary school contribution to influent loading from 0.48% to 7.00%. The percent contribution to influent loading from commercial sources did not change drastically with the increased loading from schools (Table 27). However, when examining the top three sources of mercury for each plant, secondary schools changed the distribution significantly (Figure 9). In the original calculations, secondary schools were not in the top three commercial sources of mercury, only dentists, hospitals, medical clinics and vehicle service stations contributed. When the increased loading from secondary schools was introduced, the hospital and medical clinic influence decreased as secondary schools were the second biggest source in 3 of 7 plants and the third biggest source in 2 of 7 plants. The change in maximum reduction possible (source control reduction) upon using the higher number for schools was not significant enough to change the number of plants able to meet water quality criteria using source control and pollution prevention except at Westbrook (Table 28). The change in criteria met at Westbrook is not necessarily a true representation due to the fact that source control reduction (with schools at 4.39 g/day) is 103%. This produces a less than zero grams/day influent concentration.

DOTW	Schools =	Schools =	
101 W	0.3 g/day	4.39 g/day	
NEORSD-e	48%	52%	
NEORSD-s	27%	29%	
NEORSD-w	62%	65%	
Palo Alto	51%	57%	
SRCSD	36%	36%	
Westbrook	72%	96%	
WLSSD	50%	57%	

**Table 27. Estimated Percent Contribution to Influent Loading from Commercial Sources** 



**Figure 9. Change in Top Three Commercial Sources** 

 Table 28. Change in Source Control/Regulatory Reduction (g/day) Based on Varying

 Secondary School Influent Mercury Concentrations

POTW	Schools = 0.3 g/day	Lowest Effluent Criteria Met	Schools = 4.39 g/day	Lowest Effluent Criteria Met
NEORSD-e	21.8	7.8	22.5	7.8
NEORSD-s	36.0	7.8	36.8	7.8
NEORSD-w	7.1	7.8	7.2	7.8
Palo Alto	3.7	7.8	3.7	7.8
SRCSD	38.4	7.8	39.4	7.8
Westbrook	1.4	1.3	1.6	0.2
WLSSD	2.0	7.8	2.3	7.8

Figure 10. Elevated Secondary School Value





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A few wastewater treatment authorities have attempted to identify their most significant sources of mercury in treatment plant influent separately from this study. Their estimated source loading breakdowns are shown in Figure 11 for comparison. Please note that these source loading estimates are just a few examples of the potential variation from plant to plant.



### **Figure 11. Influent Mercury Source Pies**

### **Probability-Based Model**

The impact of the assumptions made for the analysis were also assessed by estimating uncertainty and confidence limits for mercury reductions in influent and effluent through implementation of different mercury reduction strategies.

Probability-based modeling procedures were applied to the reduction estimates previously developed. The basic calculation of loads, load reductions, and influent and effluent concentrations were performed as described previously in this report. Loading values for specific mercury sources were the same as described previously, unless noted. Confidence limits for mercury concentrations and percent reductions in influent and effluent were estimated by incorporating variability for the following values in the reduction model:

• Dental loads. Variance in mean mercury concentrations from dentists is estimated by resampling (i.e., using randomly selected values from the entire data set for each iteration of the calculation) the distribution of mean mercury loads (g/dentist/day) for all dentists sampled in the SF 1992, SF 1993, NEORSD 1997, and SF 2000 studies.

- Participation factors. Variance in participation for each control strategy (e.g., BMP implementation) is estimated based on survey results where available (e.g., dental practices survey) and the number of sources in each agency. The variable participation for a control strategy is combined with the fixed estimate of mercury load reduction associated with implementing each specific control strategy to provide the total reduction in mercury loads.
- Average influent and effluent concentrations. Variance of 12-month average influent and effluent mercury concentrations is estimated by resampling the available monitoring data for each agency. A comparison between the monitoring data and the model values for influent and effluent concentrations is shown in Figures 12 and 13.
- Treatment plant removal efficiency. The probability based model accounted for the relationship between influent concentration and removal efficiency. This relationship is shown in Figure 14. Variance in mercury removal efficiency for each agency is based on an analysis of covariance (ANCOVA) model of influent and effluent data for all 7 agencies. The variance is estimated as the standard deviation of the residuals of the ANCOVA model. The data used to model these parameters is summarized in Table 29.

The mercury reduction model was run for 500 iterations for each agency and mercury reduction scenario (i.e., pollution prevention and source control program implementation). The influent and effluent mercury concentrations and percent reductions are recorded for each iteration, and the resulting data represent the distribution of mean estimates for each result. Confidence limits (95% CL) for each estimate are calculated as the 0.025<sup>th</sup> and 0.975<sup>th</sup> percentiles of the set of estimates. The accuracy of the model and adequacy of the input data are assessed by comparing the effluent and influent concentrations from the model to the distribution of 12-month averages estimated from monitoring data for each agency. A summary of the model is provided in Table 29.

### Results

The following results are provided in Appendix E for each agency and mercury reduction strategy. An example is shown in Table 30.

- Estimates of mean mercury concentrations in influent and effluent, based on the source load model and monitoring data, with 95% CL; and
- Estimates of mean reductions in mercury concentrations (and loads) in influent and effluent with 95% CL, based on the source load model.

A comparison of influent mercury levels predicted by the model before and after pollution prevention program implementation is shown in Figure 15. A comparison of effluent mercury levels predicted by the model before and after pollution prevention program implementation is shown in Figure 16. Results for the source control program showed similar variations. Mean values predicted by the model for each agency are summarized in Table 31. Average effluent reductions predicted by the model are lower than reductions calculated as part of the analysis because the model accounted for the relationship between influent concentration and plant removal efficiency. As can be seen in the figures, the results predicted by the model give a wide range of values for resulting effluent concentrations because of the variability of the data used to develop the model.

# Table 29. Summary of Probability-Based Modeling of Mercury Reductions Achievable Through Pollution Prevention and Source Control Strategies

	Pre-Pollution Prevention/Source Control Implementation		Post-Pollution Prevention Implementation		Post-Source Control Implementation	
SOURCE LOADS	Fixed Estimate	Resample Estimate	Fixed Estimate	Resample Estimate (3)	Fixed Estimate	Resample Estimate (3)
Dentists		Х		Х		Х
Medical Clinics	Х		(2)	(2)		Х
Vehicle Service		Х	(2)	(2)		Х
Hospitals		Х	(2)	(2)		Х
Universities	Х		(2)	(2)		Х
Human Waste, Amalgam	Х		Х			Х
Human Waste, Dietary	Х		Х			Х
Laundry Graywater	Х		Х			Х
Household Products	х		Х			Х
Thermometers	Х		Х			Х
Contact Lens Solution	Х		Х			Х
Industrial	(4)		(4)		(4)	

(1) Can be calculated as resampled estimate based on monitoring data.

(2) BMP reductions implemented only for 3 largest commercial sources for each agency.

(3) Post-BMP loads based on fixed percent reduction and variable participation in BMPs.

(4) Assumed that BMPs for Industrial Hg reduction already implemented for all scenarios.

INFLUENT DATA	Model Estimate	Monitoring Data	
Influent Load	Calculation: • Hg Source Loads	Not Estimated	
Avg. Hg Concentration	Calculation: • Hg Loads ÷ Mean Plant Discharge	Resampled 12-month avg. for compariso to modeled estimates	
Percent Hg Reduction	Calculation with Model estimates: 100% x (Hg <sub>Post-BMP</sub> - Hg <sub>Pre-BMP</sub> ) ÷ Hg <sub>Pre-BMP</sub>		

Treatment Efficiency	Regression Model with random error; adjusted for each agency:
(% Removal)	Ln(1-%Removal) = b Intercept + Ln[HgInf] • m + b plant + Error St.Dev,

EFFLUENT DATA	Model Estimate	Monitoring Data	
Avg. Hg Concentration	Calculation: Influent Hg x (1 - % removal)	Resampled 12-month avg. for compariso to modeled estimates	
Avg. Percent Hg Reduction	Calculation with Model estimates: (Post-BMP [Hg] - Pre-BMP [Hg]) ÷ Pre-BMP [Hg]		

Table 30. Results of Probability-Based Modeling of Mercury Reductions Achievable Through Pollution Prevention and Source Control BMP Implementation Strategies: SRCSD.

	12-Sample Mean Influent Hg, ng/L				%Reduction			
	Monitoring Data (1)	Load Model, Pre- P2/SC	Load Model, P2	Load Model, SC	P2 Program	SC Program		
Count	500	500	500	500	500	500		
Average	198	245	180	174	26.4%	32.6%		
SE	28.4	30.5	23.5	23.3	4.2%	4.2%		
LL95	149.7	189.2	138.2	134.3	18.4%	24.6%		
Median	193.5	243.9	178.5	170.5	26.5%	32.7%		
UL95	263.8	305.7	227.4	225.6	34.1%	40.3%		
Min	117.9	156.9	123.1	112.4	15.2%	21.7%		
Max	303.8	331.4	259.0	250.2	36.3%	44.1%		

12-Samp	%Reduction				
Monitoring Data (1)	Load Model, Pre- P2/SC	Load Model, P2	Load Model, SC	P2 Program	SC Program
500	500	500	500	500	500
8.7	9.7	9.4	9.0	2.4%	3.1%
0.6	5.2	5.1	4.4	0.4%	0.5%
7.5	3.2	3.1	3.2	1.6%	2.2%
8.6	8.5	8.3	8.0	2.4%	3.1%
10.0	22.4	21.9	19.5	3.3%	4.0%
7.1	2.4	2.4	1.7	1.3%	1.9%
11.1	40.3	39.5	31.7	3.5%	4.6%

(1) Estimated from resampled monitoring data distribution. P2 = Pollution Prevention SC = Source Control

Figure 12. Influent Levels Based on Monitoring Data and Load Model



Figure 13. Effluent Levels Based on Monitoring Data and Load Model



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Figure 14. Influent Concentration and Removal Efficiency

Figure 15. Influent Reduction Resulting from Pollution Prevention Implementation



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### Table 31. Average Concentrations and Reductions Predicted by Model

	Mean Influent, ng/L	Percent Reduction	Mean Effluent, ng/L	Percent Reduction
NEORSD-E	145.9	33.0%	3.1	3.2%
NEORSD-S	181.3	31.5%	3.0	3.0%
NEORSD-W	167.7	28.9%	3.2	2.7%
Palo Alto	244.1	30.3%	4.5	2.8%
SRCSD	243.9	26.5%	8.3	2.4%
Westbrook	313.8	35.9%	3.3	3.5%
WLSSD	101.5	32.6%	8.5	3.1%

#### Post-Pollution Prevention(voluntary) Influent and Effluent Qualit

#### Post-Source Control (regulatory) Influent and Effluent Quality

	Mean Influent, ng/L	Percent Reduction	Mean Effluent, ng/L	Percent Reduction
NEORSD-E	92.7	41.3%	3.2	4.2%
NEORSD-S	117.5	41.3%	3.0	4.2%
NEORSD-W	104.2	43.2%	3.0	4.4%
Palo Alto	136.1	43.1%	4.2	4.4%
SRCSD	170.5	32.7%	8.0	3.1%
Westbrook	131.1	54.5%	2.9	6.1%
WLSSD	68.9	39.4%	8.8	3.9%

# Findings

The purpose of this project was to determine if pollution prevention and/or source control programs have the potential to achieve the reductions necessary to enable POTWs to comply with current and proposed NPDES permit effluent limits for mercury. The analysis conducted was based on the use of existing data. However, a variety of assumptions were necessary to apply the collected data to the POTWs used as case studies. As a result, this analysis has certain limitations. The findings regarding the effectiveness of mercury pollution prevention programs, assessment of potential compliance, the impact of the assumptions made, and limitations of the analysis are discussed below.

# Effectiveness of Mercury Pollution Prevention and Source Control Programs

The effectiveness of mercury pollution prevention and source control programs may be considered with respect to the direct benefit of achieving reductions in wastewater influent. Mercury pollution prevention and source control programs may also achieve significant reductions to other waste streams resulting in overall reductions of mercury entering the environment. The benefits to other environmental media were not evaluated quantitatively in

this study but several reduction opportunities were identified. Effectiveness with respect to wastewater reductions and benefits to other media are discussed below.

### **Potential for Wastewater Reductions**

Using the basic scenario described in this report (i.e., setting dental discharges at 0.056 g/dentist/day and human waste from amalgam at 17  $\mu$ g/person day), the results of the analysis described above indicate the following about wastewater mercury pollution prevention programs.

Influent load reductions for mercury achievable through pollution prevention activities for the POTW case studies on average ranged from 12% to 90% depending on the agency's existing pollution prevention efforts and the extent of additional pollution prevention conducted (i.e., pollution prevention or source control programs). For agencies like the Palo Alto Regional Water Quality Control Plant, Palo Alto, California and the Western Lake Superior Sanitary District (WLSSD), Duluth, Minnesota with mature pollution prevention programs, there is not much additional reduction available because most strategies have already been implemented. For example, both agencies have worked extensively with dentists and have high rates of participation/cooperation from the dental community with respect to implementation of recommended amalgam management practices. WLSSD has close to 100% cooperation from the dental community, so their influent and effluent concentrations used in the analysis reflect this level of participation. To project any further mercury reduction, source control strategies other than voluntary implementation of best management practices (BMPs) would have to be considered (i.e., regulation, and use of amalgam separators).

Average influent mercury concentrations for the POTW case studies prior to the pollution prevention considered in this analysis ranged from 106 ng/L to 323 ng/L. Average effluent concentrations prior to the pollution prevention considered in this analysis ranged from 3.1 ng/L to 9 ng/L. Maximum effluent concentrations ranged from 5 to 29 ng/L. Influent load reductions from pollution prevention resulted not only in effluent reductions but also in biosolids reductions, which may also have positive implications for POTW operations.

The largest source of mercury in wastewater influent is discharges from dental offices. The next largest sources are domestic sources (human waste, household products, and laundry graywater) and hospitals. Of the domestic sources, human waste is considered uncontrollable and laundry graywater is considered very difficult to effectively control. Household products are controllable to the extent that residents can be persuaded to stop using them or to the extent that their availability can be restricted through product bans. Legislative efforts to restrict the availability of certain mercury containing products may prove effective in reducing discharges from household products. The sources with the greatest potential for achieving measurable reductions in wastewater influent are dental offices and hospitals.

### **Benefits to Other Media**

Another important benefit of pollution prevention programs, although not quantified in this report, is their beneficial impact on other media. Restriction or elimination of mercury-containing products (e.g., thermometers, thermostats, blood pressure cuffs) will also reduce the amount of mercury released to the environment through improper disposal as solid waste or

medical waste (and then to landfills, incinerators, or steam autoclaves). Similarly, educating the dental community regarding proper disposal of amalgam wastes will reduce the amount of these wastes that are transferred to solid waste or infectious waste (which gets incinerated or autoclaved). One finding of the San Francisco dental surveys and site inspections was that dentists believed that they were properly disposing of scrap amalgam as hazardous waste (WERF, 2001). However, the site inspections revealed that many of them were disposing of amalgam wastes as biohazardous/medical waste. The result of this was that, while disposal to the sewer was prevented, the ultimate release of the mercury would be through incineration to the air. As a result of this finding, education of dentists has included the message to dispose of amalgam through certified recyclers and not as medical waste. While no additional reductions in wastewater are likely to be achieved by this action, the overall release of mercury to the environment will be reduced. This reduction depends on the proper recycling mechanism being available. Local agencies can help accomplish this by identifying recyclers and providing this information to the appropriate businesses.

Other indirect benefits of wastewater source control and pollution prevention programs include increasing public awareness of mercury pollution issues and the potential to create partnerships with other agencies that have more direct control over certain waste streams and established communication vehicles. Increased public awareness may result in more successful legislative activity at both the state and federal level. Working with other agencies and businesses (i.e., health departments, solid waste programs, air programs, recycling companies, environmental organizations, etc.) may result in more widespread communication to both the general public and the business community that may result in behavior changes that achieve reductions in environmental releases.

The Wisconsin Department of Natural Resources (WDNR) has been working with municipalities and is developing a Municipal Mercury Pollutant Minimization Program to help agencies comply with the GLI mercury effluent requirements (Case, 2001). The program's goals include reducing mercury use through promotion of alternative products and reducing mercury releases through recycling and improved waste management. Program elements include establishing partnerships and working with a variety of mercury sources including medical facilities, dental clinics, secondary schools, colleges, industry and the general public. Effectiveness measurement is an important element of the program.

The program is based on over 4 years of pilot work with municipal agencies. The pilot work has already shown that municipal mercury reduction activities will have benefits beyond wastewater reductions. As a result, WDNR is exploring approaches to provide POTWs with credit for benefits to other media as an offset against final effluent discharge compliance. Another added benefit recognized by WDNR is that outreach activities often reach audiences outside of a POTW's service area. WDNR is exploring approaches to provide some type of credit for this benefit as well.

### Compliance Assessment

While measurable reductions are expected as a result of mercury pollution prevention programs, these reductions do not appear to have a significant impact on a POTW's ability to comply with

the more stringent effluent limits evaluated in this study. However, pollution prevention or source control may result in adequate reductions to achieve permit limits under certain circumstances (i.e., reduction needed is reasonable, as in the case of achieving the 7.8 ng/L limit developed from the fish tissue criterion using default values). For limits based on the CTR (i.e., 25 ng/L), or other less stringent criteria (i.e., based on fish tissue criterion for rivers and streams, 17-18 ng/L), the case study POTWs could generally comply prior to implementing pollution prevention. For the Great Lakes Criteria (i.e., 1.3 ng/L), none of the POTWs were able to comply even after the estimated reductions based on pollution prevention (all voluntary) efforts were calculated. One agency was able to comply on the basis of a source control/semi-regulatory program. For the intermediate standard of 7.8 ng/L, the two POTWs that could not comply prior to pollution prevention were projected to be able to achieve that level after the implementation of a source control/semi-regulatory program.

One of the limitations of this study is that it is theoretical in nature. There are very few examples of mercury source control programs that have been in place long enough to yield measurable results. However, some examples that may give an indication of the potential effectiveness of mercury pollution prevention and source control programs include the programs implemented by the Palo Alto Regional Water Quality Control Plant, Palo Alto, California, the Western Lake Superior Sanitary District (WLSSD), Duluth, Minnesota, and Metropolitan Council Environmental Services (MCES), St. Paul, Minnesota, and experiences in Denmark.

As noted previously, WLSSD and Palo Alto have both implemented most, if not all, of the recommended pollution prevention strategies described in this analysis. Source control strategies that have not been implemented include regulating dentists and requiring amalgam separators. Neither of these POTWs is able to consistently achieve effluent concentrations below 3.1 ng/L. Palo Alto's reported maximum and average effluent concentrations were 18.3 ng/L and 5.5 ng/L respectively and WLSSD reported maximum and average effluent concentrations of 29 ng/L and 4.7 ng/L respectively. Therefore, in these two communities pollution prevention has not been able to achieve very low mercury effluent levels.

MCES conducted a study, in cooperation with the Minnesota Dental Association, to assess the reduction of mercury levels in biosolids resulting from the installation and operation of amalgam removal equipment in dental clinics (Anderson, 2001). MCES obtained baseline data for mercury loadings in biosolids for two treatment plants (Hastings and Cottage Grove). Amalgam removal equipment was then installed in all the dental clinics in the Hastings service area and all but one dental clinic in the Cottage Grove service area. Mercury biosolids levels dropped 44% and 29% for the Hastings and Cottage Grove treatment plants respectively during the period when the removal equipment was in operation at the dental clinics. Because influent and effluent monitoring were not conducted for this study, no information is presented regarding the impact of amalgam removal equipment on treatment plant effluent levels of mercury. However, operation of amalgam removal equipment by dentists appears to have the potential to reduce biosolids mercury levels.

In Denmark, several POTWs have required that dentists in their service area to install amalgam separators (Arenholt-Bindslev, 1999). Agencies were surveyed in 1999 to assess the

effectiveness of this strategy with respect to mercury reductions. Out of 273 counties surveyed, 174 indicated that amalgam separators had been installed in all dental offices in the service area. Of these counties, 45 provided adequate data to calculate reductions in mercury levels in treatment plant biosolids after the separators had been installed. Reductions for 33 of the plants providing data are compared to initial mercury biosolids levels in Figure 17. Approximately half of the agencies observed no statistically significant change in biosolids concentrations after the installation of amalgam separators. Reductions ranged from 14% to 80% for those agencies experiencing measurable reductions (other than the one value at 14%, the range of the data was 32% to 80%). There appears to be some correlation between initial biosolids levels (i.e., prior to installation of amalgam separators) and reduction achieved. Many of the Danish areas observing no significant changes in biosolids concentrations had relatively low initial levels. No data was reported regarding effluent levels. However, because of the particulate nature of amalgam, it is likely that reductions in effluent were no greater than reductions seen in the biosolids. An 80% reduction would not be adequate for most of the agencies in this study to achieve the most stringent effluent limits (i.e., 1.3 ng/L or lower). The Danish results indicate that the effectiveness of regulation and amalgam separators is highly variable. While significant measurable reductions were achieved in some cases, other cases resulted in no significant change.

Figure 17. Biosolids Mercury Reductions for 33 Danish Counties After Amalgam Separator Installation



The controllability of influent sources and the effectiveness of voluntary programs ultimately impact a POTW's ability to meet the more stringent effluent limits. As noted previously, pollution prevention is based on voluntary actions. While regulatory approaches may be available for commercial sources, they are labor intensive and therefore only cost effective for the largest sources (i.e., dentists). Regulatory approaches are not available for residential activities because POTWs lack the legal authority to regulate domestic users. In addition, some domestic sources are essentially uncontrollable (i.e., human waste). Product bans are one

approach being explored in several states, but their impact on wastewater levels of mercury remains to be seen. Overall there is a limit to the potential effectiveness of pollution prevention. On average, residential sources accounted for approximately 25% of the influent loading. Therefore, even if commercial and industrial mercury discharges could be completely eliminated, the maximum reduction achievable is about 75%. As noted above, for the more stringent effluent limits, reductions greater than 75% are needed for most agencies to consistently meet these levels.

The estimated annual cost of the pollution prevention program ranged from \$250,000 to \$350,000 depending on the size of the service area. The estimated annual cost of the source control program ranged from \$300,000 to \$700,000. Because pollution prevention was not adequate to achieve consistent compliance with 1.3 ng/L, additional POTW treatment would also be necessary. The annual total cost of this additional treatment ranged from \$1.2 to \$226 million per POTW depending on the size of the POTW and the reduction needed. Interestingly, the cost of treatment without pollution prevention was not significantly different, ranging from \$4.8 to \$300 million annually.

### Impact of Assumptions

The assumptions that impacted the results most heavily were the values assumed for dental discharges and human waste associated with amalgam and the assumptions regarding percentage removals through POTWs. While the values assumed for the first two parameters had a significant impact on the estimated load reductions and resulting effluent concentrations, they did not have a significant impact on the ability of POTWs to comply with effluent limits or the estimated cost to comply with these limits. Regardless of the values chosen, dental discharges accounted for the largest portion of influent loadings and, therefore, represent the source for which pollution prevention and source control efforts would be expected to be most effective with respect to measurable reductions. The percent removals of mercury at each plant need to be studied in more depth. It is difficult to predict the concentration of mercury in the effluent based on the concentration in the influent. As noted in the discussion regarding the probability-based model, there is some indication that as influent concentrations decrease, the percent removal in the effluent also decreases. The method for determining effluent from influent in this study was the most reasonable available method.

# Limitations of Analysis

As noted previously, several assumptions were incorporated into the estimate of effluent mercury reductions achievable through pollution prevention. These limitations are listed below:

• Dental discharge data is primarily the liquid fraction of mercury measured in the lateral leaving the dental facility. While these values were measured as total mercury, they may underestimate the amount of mercury that leaves the dental facility each day, because some of the mercury (as amalgam) will settle out and may leach back into the water at a later date. Other studies, as noted previously, have estimated that larger amounts of mercury may be discharged from dental offices. However, for the purposes of this calculation, a conservative estimate of the amount of mercury that reaches the treatment plant is used. It is assumed that this is best represented by the mercury in the liquid fraction (both smaller amalgam

particulates and dissolved) leaving the dental facility but this would need to be confirmed by further monitoring and research.

- The mercury levels from human waste are based on measurements of the human waste itself rather than the amount in the wastewater stream. These measurements are for total mercury, which may overestimate the amount that reaches the treatment plant influent.
- There is some uncertainty regarding total and dissolved mercury measurements and analytical techniques used for the measurements made both by the case study POTWs and by the agencies conducting analysis of sources that were used in this report. These uncertainties may decrease the confidence level associated with the mass balances. For instance, the 7470 digestion method, typically used for wastewater analysis, does not dissolve larger particles of amalgam and, therefore, would not generate an accurate measure of the mercury content. This is a concern for samples that are high in amalgam solids. However, the digestions used for wastewater dental samples (if they have relatively low solids content) are aggressive enough to dissolve the amalgam in the particles in these samples.
- The uncertainties regarding the form of mercury (i.e., particulate vs. dissolved) may also impact the levels of mercury estimated in the POTW influent and effluent and may, therefore, affect the mass balance determinations. It may also impact the effectiveness of source control programs and other efforts seeking to reduce mercury effluent levels. If mercury is reaching the plant as larger particulates, it is likely to be removed in the grit chambers or it will enter the biosolids, not the effluent. Source control efforts that remove larger solids will not necessarily have much impact on influent and effluent levels. However, removal of larger particles still meets the goal of reducing release of mercury into the environment. Overall, the form of mercury and how this affects its movement through the treatment plant requires further study to accurately predict the relationship between source control and effluent reductions.

Regardless of these limitations, discharges from dentists appear to represent the largest contributor to mercury influent levels. Human waste, while a significant source, represents a small contribution relative to dentists.

Another limitation of this analysis is the use of average removal efficiencies when calculating effluent concentrations based on influent reductions. As noted, there is some indication that POTW removal efficiencies will decrease as influent concentration decreases. The probability-based model, for example, predicts much lower effluent reductions than influent reductions. A better correlation between removal efficiency and influent concentrations could increase the accuracy of this analysis.

This report only attempts to quantify mercury reductions in effluent and, to some extent, in biosolids. Other reductions in environmental releases of mercury were only evaluated qualitatively. It is possible that the reductions in releases to other media are equally significant and may merit further evaluation.

It must be recognized that this study was geared towards creating an 'average' community, in terms of size and potential sources of mercury. Some communities, especially smaller ones, may

be more heavily influenced by sources such as schools and laboratories that were considered to be a small influence in the 'average' community approach.

This report is a theoretical study on the impacts of mercury source control efforts on POTW effluents. As noted above, there is very little experimental verification of predicted results because few POTWs have conducted extensive mercury source control programs over a long enough time period to determine the level of reduction that is achievable. For other pollutants, POTWs have found that, over a period of years, pollution prevention and source control can achieve significant reduction under the right circumstances (WERF, 2000).

# Conclusions

The results of this study indicate that mercury source control and pollution prevention programs have the potential to achieve measurable reductions in POTW influent and to have positive impacts with respect to reducing other environmental releases of mercury. Source control and pollution prevention may also be effective in helping POTWs achieve effluent limits assuming the required reduction falls within a specific range. The results of this study indicated that, based on the assumptions made, pollution prevention or source control are potentially effective in achieving sufficient reductions to enable POTWs to meet effluent limits that are 7.8 ng/L or greater. However, if more stringent effluent limits are in effect such as the 3.1 or 1.3 ng/L limits that have been imposed on POTWs in the Great Lakes Region, pollution prevention or source control with no treatment process modifications will not be effective in achieving these limits.

Regardless of the potential for meeting effluent limits through pollution prevention and source control alone, these efforts have many benefits as described in this report and should be considered as an essential tool in any mercury reduction effort. Reduction of mercury at its sources will have positive impacts for wastewater influent and biosolids and for other media.

Pollution prevention efforts targeting sources of mercury should focus on dental offices and medical facilities (hospitals) to have the greatest potential for achieving measurable reductions. With respect to dental offices, implementation of BMPs, such as good housekeeping and proper management of existing filters, should be required as the initial approach. However, if additional reductions are needed, regulatory approaches and the required installation of treatment should be considered. For hospitals and medical facilities, implementation of BMPs and purchasing policies promoting non-mercury containing items has proven effective with respect to reducing mercury wastewater discharges from these facilities.

# Recommendations

Areas requiring further study to obtain a better understanding of mercury sources and the potential for reductions were identified in this report and include:

• Additional study of the relationship between influent mercury concentrations and removal efficiencies through the treatment plant would help clarify the relationship between influent reductions and resulting effluent concentrations. Present data shows that the relationship is not linear. Additional study also is needed with respect to the portion of mercury present in wastewater in solid form and in liquid form. The form of mercury present in wastewater will

have a significant impact on its travel through the treatment process and the reductions that are ultimately achievable as a result of source control and pollution prevention efforts.

- To gain a more complete understanding of mercury sources in wastewater treatment plant influent, a more comprehensive effort to assess total mercury discharges from dental offices should be conducted. In addition, research that more directly measures mercury in wastewater resulting from human wastes should be conducted.
- To further assess the feasibility of reducing mercury levels in laundry graywater, research could be conducted to ascertain the origin of mercury in the graywater (i.e., does it come from dirt or clothing dyes).
- Recommended practices for larger sources such as dentists may have a significant impact on the magnitudes of reductions achievable by these sources. Certain practices will have greater impacts than others will. For example, attention should be given to screenings disposal/handling at dental offices. It would be helpful to have a standard protocol for disposal/handling and to get cooperation from state agencies to aid in disposal to facilitate implementation of BMPs by dentists and other sources.
- Additional monitoring and evaluation of discharges from schools should be conducted to determine if this is a significant mercury source. There is some indication that schools with laboratories have the potential to discharge significant quantities of mercury.

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