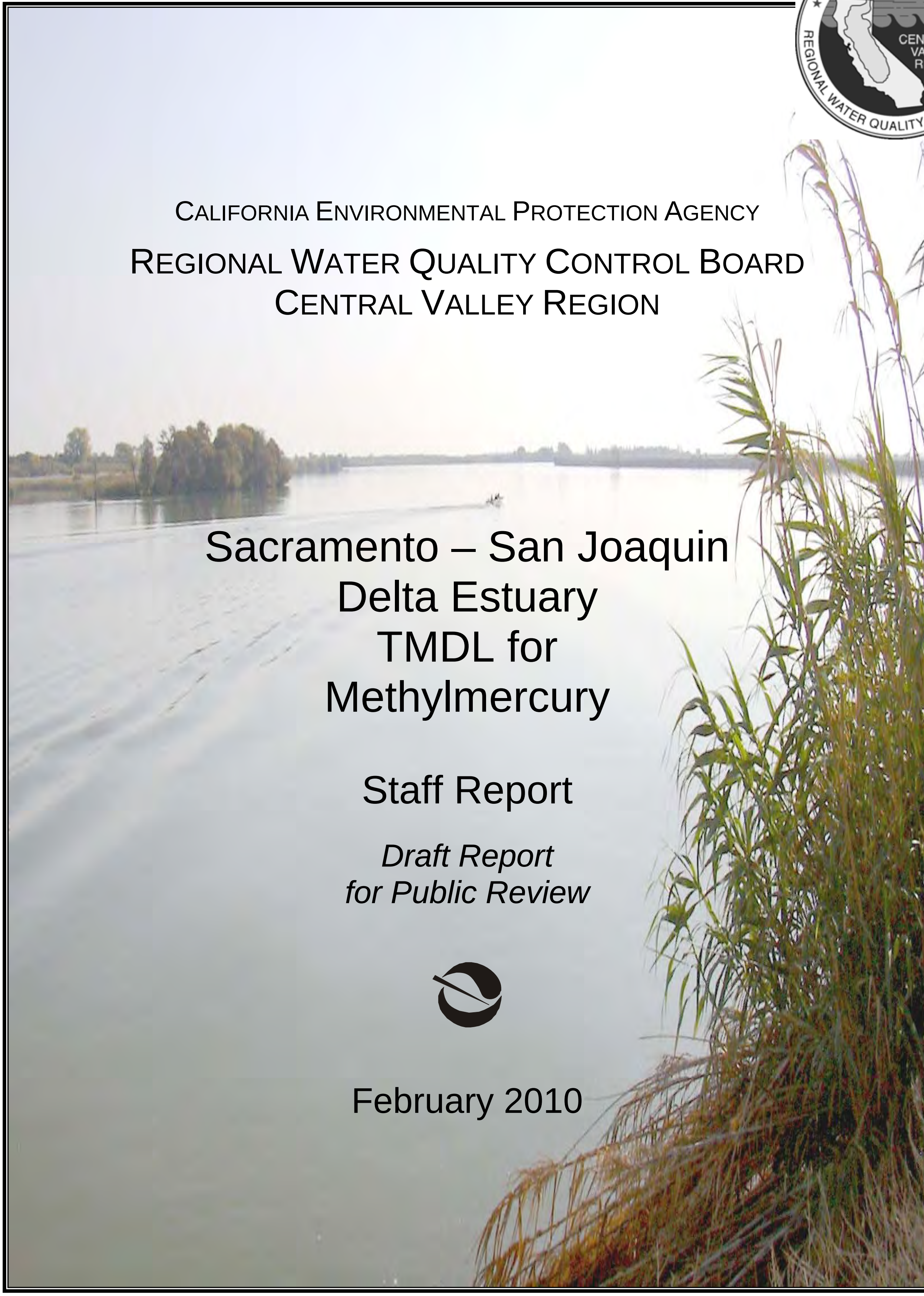

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

Sacramento – San Joaquin Delta Estuary TMDL for Methylmercury

Staff Report

Draft Report for Public Review

February 2010

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DISCLAIMER
This publication is a report by staff of the California Regional Water Quality Control Board, Central Valley Region. This report contains the evaluation of alternatives and technical support for the adoption of a Basin Plan Amendment to the Water Quality Control Plan for the Sacramento and San Joaquin River Basins (Resolution No. TBD). Mention of specific products does not represent endorsement of those products by the Central Valley Water Board.

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SACRAMENTO – SAN JOAQUIN DELTA ESTUARY TMDL FOR METHYLMERCURY

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EXECUTIVE SUMMARY

This draft report presents California Regional Water Quality Control Board, Central Valley Region (Central Valley Water Board) staff recommendations for establishing a Total Maximum Daily Load (TMDL) for methylmercury in the Sacramento-San Joaquin Delta Estuary (the Delta). The report contains an analysis of the mercury impairment, a review of the primary sources, a linkage between methylmercury sources and impairments, and recommended mercury reductions to eliminate the impairment.

This TMDL report is one component in the Central Valley Water Board's water quality attainment strategy to resolve the mercury impairment in the Delta. The second component is implementing a control program through amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (the Basin Plan), as described in the proposed Basin Plan amendments and text in the draft Basin Plan Amendment staff report.

Scope, Numeric Targets & Extent of Impairment

In 1990 the Central Valley Water Board identified the Delta as impaired by mercury because fish had elevated levels of mercury that posed a risk for human and wildlife consumers. As a result, the Delta methylmercury TMDL addresses all waterways within the legal Delta boundary. In addition, the San Francisco Bay Regional Water Quality Control Board (San Francisco Water Board) identified Central Valley outflows *via* the Delta as one of the principal sources of total mercury to San Francisco Bay and, in its 2006 mercury TMDL for San Francisco Bay, assigned the Central Valley a load reduction of 110 kg/yr. Therefore, the final mercury TMDL control plan for the Delta must ensure protection of human and wildlife health in the Delta and meet the San Francisco Bay TMDL load allocation for the Central Valley.

This TMDL report addresses both methyl and total mercury sources. Reductions in ambient aqueous methylmercury and methylmercury sources are required to reduce methylmercury concentrations in fish. The methylmercury linkage and source analyses divide the Delta into eight subareas based on the hydrologic characteristics and mixing of the source waters. Because the Yolo Bypass acts as a substantial source of methylmercury and total mercury to the Delta, the entire Yolo Bypass was included in the Yolo Bypass subarea. The Yolo Bypass is a 73,300-acre floodplain on the west side of the lower Sacramento River, about two thirds of which is within the legal Delta boundary.

A separate methylmercury allocation scheme was developed for each subarea because the levels of impairment and the methylmercury sources in the subareas are substantially different. Reductions in total mercury loads are needed to reduce aqueous methylmercury in the Delta, to maintain compliance with the USEPA's criterion of 50 ng/l, and to comply with the San Francisco Bay mercury control program.

The concentration of methylmercury in fish tissue is the type of numeric target selected for the Delta methylmercury TMDL. Acceptable fish tissue levels of methylmercury for the trophic level (TL) food groups consumed by piscivorous wildlife species (that is, species that feed on fish) were calculated using a method developed by the U.S. Fish and Wildlife Service that uses daily intake levels, body weights and consumption rates. Numeric targets were developed to protect humans in a manner analogous to targets for wildlife using a method approved by the U.S. Environmental Protection Agency and Delta-specific information.

Three numeric targets are recommended for the protection of humans and piscivorous wildlife: 0.24 mg/kg (wet weight) in muscle tissue of large[1] trophic level four (TL4) fish such as bass and catfish; 0.08 mg/kg (wet weight) in muscle tissue of large TL3 fish such as carp and salmon; and 0.03 mg/kg (wet weight) in whole TL2 and TL3 fish less than 50 mm in length. The targets for large TL3 and TL4 fish are protective of (a) humans eating 32 g/day (8 ounces, uncooked fish per week) of commonly consumed, large fish; and (b) all wildlife species that consume large fish. The target for small TL2 and TL3 fish is protective of wildlife species that consume small fish.

Elevated fish methylmercury concentrations occur along the periphery of the Delta while lower body burdens occur in the central Delta. Concentrations are greater than recommended as safe by the USFWS for wildlife in all subareas except in the Central Delta subarea. The Central Delta subarea requires no reduction to meet the proposed large TL3 fish target for human protection and an 8% reduction to meet the proposed large TL4 fish target for human protection. Percent reductions in fish methylmercury levels ranging from 0% to 75% in the peripheral Delta subareas will be needed to meet the numeric targets for wildlife and human health protection.

Linkage

The Delta linkage analysis focuses on the comparison of methylmercury concentrations in water and biota. Statistically significant, positive correlations have been found between aqueous methylmercury and aquatic biota, indicating that methylmercury levels in water is one of the primary factors determining methylmercury concentrations in fish.

The Delta TMDL linkage focuses on the correlation between aqueous methylmercury and largemouth bass methylmercury because (1) largemouth bass was the only species systematically collected near many of the aqueous methylmercury sampling locations used to develop the methylmercury mass balance for the Delta (next section) and (2) largemouth bass is a useful bioindicator of spatial variation in mercury accumulation in the aquatic food chain because it maintains a localized home range and has a high trophic position in the Delta food web. It was possible to describe the recommended fish tissue targets in terms of the mercury concentration in standard 350 mm largemouth bass. A methylmercury concentration of 0.28 mg/kg in 350 mm largemouth bass is equivalent to the target of 0.24 mg/kg for large TL4 fish. A methylmercury concentration of 0.24 mg/kg in 350 mm largemouth bass is equivalent to the target of 0.08 mg/kg for TL3 fish. A methylmercury concentration of 0.42 mg/kg in 350 mm largemouth bass is equivalent to the target of 0.03 mg/kg for small fish. The methylmercury

[1] Large fish are defined as 150-500 mm total length or legal catch length if designated by CDFG.

concentration of 0.24 mg/kg in bass predicted for the TL3 fish tissue target is the lowest of the bass values predicted for the three fish tissue targets and is therefore most likely protective of both human and wildlife consumers of higher and lower trophic level fish in the Delta. As a result, a methylmercury concentration of 0.24 mg/kg in 350 mm largemouth bass is referred to as the recommended implementation goal for largemouth bass.

The mercury concentrations in standard 350-mm largemouth bass for each Delta subarea were regressed against the average unfiltered methylmercury concentrations in water in each Delta subarea. Substitution of the recommended implementation goal for largemouth bass (0.24 mg/kg) into the equation developed by this regression results in a predicted, average safe methylmercury concentration in ambient water of 0.066 ng/l. Incorporation of an explicit margin of safety of about 10% results in the recommended implementation goal for unfiltered ambient water of 0.06 ng/l methylmercury. This implementation goal would be applied as an annual average methylmercury concentration in ambient waters of the Delta. The recommended implementation goal is currently met in the Central Delta subarea and nearly met in the West Delta subarea.

Sources – Methylmercury

Average annual methylmercury inputs and exports were estimated for water years (WY) 2000 to 2003, a relatively dry period that encompasses the available information. Sources of methylmercury in Delta waters include tributary inputs from upstream watersheds and within-Delta sources such as methylmercury flux from wetland and in-channel sediments, municipal and industrial wastewater, agricultural drainage, and urban runoff. Losses include water outflow to San Francisco Bay, exports to southern California, removal of dredged sediments, photodegradation, uptake by biota, and particle settling. Figure 1 illustrates the average daily methylmercury imports to and exports from the Delta and Yolo Bypass. Methylmercury flux from wetland and open water sediments within the Delta and Yolo Bypass accounts for about 35% of methylmercury inputs to the Delta/Yolo Bypass. Tributaries contribute about 58% of the Delta/Yolo Bypass methylmercury inputs. The difference between the sum of known inputs and exports is a measure of the uncertainty of the loading estimates and of the importance of other loss processes at work in the Delta. The sum of known water inputs and exports for WY2000-2003 balances to within about 5%, indicating that all the major water inputs and exports have been identified. In contrast, the methylmercury budget for WY2000-2003 does not balance. Average annual methylmercury inputs and exports were approximately 14.3 g/day (5.2 kg/yr) and 6.7 g/day (2.5 kg/yr), respectively (Figure 1). Exports were only about 50% of inputs, indicating that the Delta acts as a net sink for methylmercury. Later studies have shown that methylmercury photodegradation and particle settling can account for this with-Delta loss.

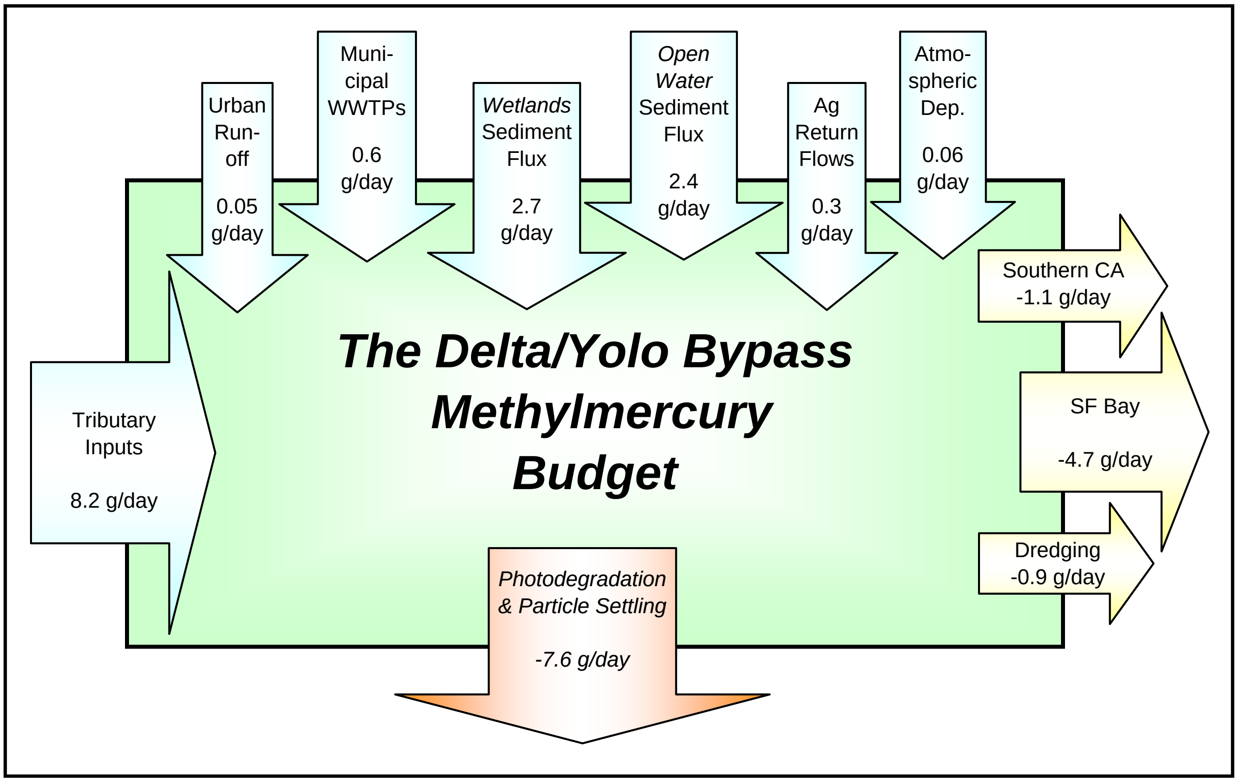

Figure 1: Average Daily Methylmercury Inputs to and Exports from the Delta/Yolo Bypass.

Sources – Total Mercury & Suspended Sediment

Sources of total mercury in the Delta and Yolo Bypass include tributary inflows from upstream watersheds, atmospheric deposition, urban runoff, and municipal and industrial wastewater. More than 97% of identified total mercury loading to the Delta/Yolo Bypass comes from tributary inputs; within-Delta sources are a very small component of overall loading. Losses include outflow to San Francisco Bay, water exports to southern California, removal of dredged sediments, and evasion.

The Sacramento Basin, which is comprised of the Sacramento River and Yolo Bypass tributary watersheds, contributes 80% or more of total mercury fluxing through the Delta. Of the watersheds in the Sacramento Basin, the Cache Creek and upper Sacramento River (above Colusa) watersheds contribute the most mercury. The Cache Creek, Feather River, American River, and Putah Creek watersheds in the Sacramento Basin, and the Cosumnes River in the San Joaquin Basin, have both relatively large mercury loadings and high mercury concentrations in suspended sediment, which makes these watersheds attractive candidates for load reduction programs.

Methylmercury Allocations & Total Mercury Limits

Methylmercury allocations were made in terms of the existing assimilative capacity of the different Delta subareas. To determine how much methylmercury in ambient Delta waters need to be reduced to achieve the proposed fish targets, the existing average methylmercury concentration in water in each Delta subarea was compared to the proposed methylmercury goal for ambient water (0.06 ng/l). The amount of reduction needed in each subarea is expressed as a percent of the ambient concentration. Percent reductions required in order to meet the goal ranged from 0% in the Central Delta subarea to about 80% in the Yolo Bypass and Mokelumne River subareas.

In order to achieve the proposed fish targets in each Delta subarea, loads of methylmercury from within-Delta point and nonpoint sources and tributary inputs need to be reduced in proportion to the desired decrease in concentrations needed for ambient waters to meet the proposed goal. The percent reductions and allocations were calculated as percentages of existing loads. The percent reductions vary by subarea because the percent reductions required for ambient water methylmercury levels in each subarea to meet the proposed methylmercury goal vary. No reductions were recommended for sources to the Central and West Delta because the fish and water methylmercury levels achieve or almost achieve the proposed numeric targets and implementation goals, and because methylmercury levels are expected to decrease in these subareas as control actions take place upstream. Percent reductions were applied to point and nonpoint source loads within other subareas, except those sources that act as dilution (i.e., have existing average methylmercury concentrations at or below the proposed methylmercury goal of 0.06 ng/l). No individual point source would be expected to reduce its discharged methylmercury concentrations to below the proposed implementation goal (or, for nonpoint sources, below their intake water methylmercury concentrations).

A total mercury load reduction strategy was developed to comply with the San Francisco Bay mercury control program, to maintain compliance with the USEPA's criterion of 50 ng/l, and to help reduce aqueous methylmercury in the Delta. Staff applied the San Francisco Bay TMDL's allocated reduction of 110 kg total mercury reduction to tributary inputs to the Delta/Yolo Bypass because within-Delta sources comprise only a couple percent of total mercury inputs. Initial mercury reduction efforts should focus on the watersheds that export the largest volume of highly contaminated sediment such as the Cache Creek, Feather River, American River, Cosumnes River, and Putah Creek watersheds. Chapter 4 of the draft Basin Plan Amendment staff report describes additional strategies for minimizing increases from total mercury sources.

The methylmercury allocations and total mercury limits described in this report reflect the preferred implementation alternative described in Chapter 4 of the draft Basin Plan Amendment staff report and are designed to address the beneficial use impairment in all areas of the Delta and to comply with the total mercury allocation assigned by the San Francisco Bay TMDL. However, as described in the draft Basin Plan Amendment staff report, a number of alternatives are possible. The Central Valley Water Board will consider a variety of mercury reduction strategies and implementation alternatives as part of the Basin Plan amendment process. All Central Valley Water Board regulatory actions will be taken during public hearings.

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ACRONYMS

§	Section
ARB	California Air Resources Board
AWQC	Ambient water quality criterion
BAF	Bioaccumulation factor
Basin Plan	Central Valley Region Water Quality Control Plan for the Sacramento River and San Joaquin River Basins
bwt	Body weight
CCSB	Cache Creek Settling Basin
CDEC	California Data Exchange Center
CDFG	California Department of Fish and Game
CDHS	California Department of Health Services, re-organized in 2007 and renamed "California Department of Health" (CDPH). Reports issued before the 2007 re-organization are cited as "CDHS" reports.
CDPH	California Department of Health
CEIDARS	California emission inventory department and reporting system
cfs	Cubic feet per second
CFSII	Continuing survey of food intake by individuals
CMP	Coordinated Monitoring Program
CSS	Combined Sewer system
CTR	California Toxics Rule
CVP	Central Valley Project
CVRWQCB	Central Valley Regional Water Quality Control Board (a.k.a. Central Valley Water Board)
CWA	Federal Clean Water Act
df	Degrees of freedom (for statistical analyses)
DMC	Delta Mendota Canal
DTMC	Delta Tributaries Mercury Council
DWR	California Department of Water Resources
EC	Electrical conductivity
FCM	Food chain multipliers
GIS	Geographic Information System
HCI	Hydrologic Classification Index
Hg	Mercury
IEP	Interagency Ecological Program
IRIS	Integrated Risk Information System
LMB	Largemouth bass
LOAEC's	Lowest observed adverse effect concentrations
MCL	California/USEPA drinking water standards maximum contaminant levels
MDN	Mercury Deposition Network
mgd	Million gallons per day
MeHg	Monomethyl mercury (also referred to as methylmercury in this report)
MS4	Municipal Separate Storm Sewer System

ACRONYMS, *continued*

NA	Not applicable
NADP	National Atmospheric Deposition Program
NAS	National Academy of Sciences
NEMD	Natomas East Main Drain
NPDES	National Pollutant Discharge Elimination System
NPS	Nonpoint source
NWI	National Wetland Inventory
O	Oxygen
o/oo	Parts per thousand (salinity)
OBS	Optical back scatter
OEHHA	Office of Environmental Health Hazard Assessment
RFD	Reference dose
RSC	Relative source contribution
San Francisco Water Board	San Francisco Bay Regional Water Quality Control Board
SFBADPS	San Francisco Bay Atmospheric Deposition Pilot Study
SFEI	San Francisco Estuary Institute
SRCSD	Sacramento Regional County Sanitation District
SRWP	Sacramento River Watershed Program
State Board	State Water Resources Control Board (also shown as SWRCB in reference citations)
Subwatershed	Portion of watershed that is either upstream or downstream of the most-downstream major dam
SWIM	Surface water information
SWP	State water project
SWRCB	State Water Resources Control Board
TDSL	Total diet safe level
TL	Trophic level
TLR	Trophic level ratios
TMDL	Total Maximum Daily Load
TSS	Total suspended solids
USACE	U.S. Army Corps of Engineers
USBR	U.S. Bureau of Reclamation
USEPA	U.S. Environmental Protection Agency
USFDA	U.S. Food and Drug Administration.
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
ww	Wet weight concentration (e.g., for fish tissue mercury concentrations)
WWTP	Wastewater treatment plants
X2	Location in the Estuary with 2-o/oo bottom salinity

UNITS OF MEASURE

µg	microgram
µg/g	microgram per gram
µg/l	microgram per liter
µm	micrometer
cfs	cubic feet per second
cm	centimeter
g	Gram
g/day	gram per day
g/l	gram per liter
in/yr	inches per year
kg	kilogram
l	liter
m	meter
mg	milligram
mg/g	milligram per gram
ml	milliliter
mm	millimeter
ng	nanograms
ng/l	nanograms per liter
o/oo	parts per thousand (salinity)
ppb	parts per billion; usually µg/kg
ppm	parts per million; usually mg/kg or µg/g
ppt	parts per trillion; usually ng/kg

1 INTRODUCTION

This draft report presents Central Valley Regional Water Quality Control Board (Central Valley Water Board) staff recommendations for establishing a Total Maximum Daily Load for methylmercury in the Sacramento-San Joaquin Delta Estuary (Figure 1.1). The report contains an analysis of the mercury impairment, a discussion of the primary sources, a linkage between sources and impairments, and recommended methyl and total mercury reductions to eliminate the impairment. The report is one component in the Central Valley Water Board's water quality attainment strategy to resolve the mercury impairment in the Delta.

The Federal Clean Water Act (CWA) requires states to identify water bodies that do not meet their designated beneficial uses and to develop programs to eliminate impairments. States refer to the control program as a Total Maximum Daily Load (TMDL) program. A TMDL is the total maximum daily load of a pollutant that a water body can assimilate and still attain beneficial uses. The Central Valley Regional Water Quality Control Board determined in 1990 that the Delta was impaired because fish had elevated levels of mercury that posed a risk for human and wildlife consumers. In addition, the San Francisco Bay Regional Water Quality Control Board (San Francisco Water Board) identified Central Valley outflows via the Delta as one of the principal sources of total mercury to San Francisco Bay and assigned the Central Valley a load reduction (Johnson and Looker, 2004; SFBRWQCB, 2006). Therefore, the final mercury TMDL control plan for the Delta must ensure protection of human and wildlife health in the Delta and meet the San Francisco Bay load allocation to the Central Valley.

In order to meet state and federal requirements, the TMDL development process must include compiling and considering available information and appropriate analyses relevant to defining the impairment, identifying sources, and assigning responsibility for actions to resolve the impairment. This report has the following sections that reflect the key elements of the Delta methylmercury TMDL development process:

- Chapter 2 – Problem Statement: Presents information that explains the overall regulatory framework for this TMDL, lists future milestones and describes the extent of mercury impairment in the Delta.
- Chapter 3 – Controllable Processes: Describes the methylation processes that are potentially controllable in the Delta. The concepts summarized in this chapter guided the development of the methylmercury TMDL for the Delta, particularly the linkage analyses (Chapter 5), methyl and total mercury source analyses (Chapters 6 and 7), and methylmercury allocation and implementation strategies described in Chapter 4 of the draft Basin Plan Amendment staff report.
- Chapter 4 – Numeric Targets: Proposes numeric targets for fish, which, if met, would protect beneficial uses of Delta waters.
- Chapter 5 – Linkage Analysis: Describes the mathematical relationship between aqueous methylmercury concentrations and the proposed numeric targets for fish mercury levels, which is used to determine an aqueous methylmercury goal that guides the allocation of methylmercury source reductions within the statutory Delta boundary and tributary inputs.
- Chapters 6 & 7 – Source Assessment: Identifies and quantifies concentrations and loads of methyl and total mercury sources.

- Chapter 8 – Allocations: Presents recommended methylmercury allocations and total mercury limits for Delta sources to reduce methylmercury concentrations in fish and to comply with the USEPA's CTR and the San Francisco Bay Mercury TMDL allocation for total mercury leaving the Central Valley watershed. This chapter also describes the margin of safety afforded by the analyses' uncertainties and consideration of seasonal variations.

Since the June 2006 draft TMDL Report issued for scientific peer review, staff made several changes to the TMDL Report in response to comments made by the scientific peer reviewers and other agencies and stakeholders, as reflected in the February 2008 draft TMDL Report:

- Expansion of the numeric target evaluation (Chapter 4) to include results from recent interviews of local community-based groups and pilot surveys and recent final and draft fish mercury advisories for the Delta region.
- Expansion of the methylmercury source analysis (Chapter 6) and methylmercury allocation scheme (Chapter 8) to include methylmercury inputs to the portion of the Yolo Bypass that is north of the legal Delta using methods evaluated and found acceptable by the scientific peer reviewers. About 72% of the 73,300-acre Yolo Bypass is within the legal Delta boundary. Previous analyses indicated that the Yolo Bypass is a substantial source of methylmercury to the Delta, such that it makes sense to expand the methylmercury allocation scheme for the legal Delta to include the northern Yolo Bypass. Sacramento and Feather Rivers (via Fremont and Sacramento Weirs), Cache Creek, Willow Slough, and the Knights Landing Ridge Cut from the Colusa Basin all drain directly to the Yolo Bypass north of the legal Delta. Sources within the northern Yolo Bypass include wetlands and open water habitats, two WWTP discharges, agricultural lands, and a small amount of urbanized land. The 2006 draft TMDL Report included methylmercury allocations for sources within 30 miles of the legal Delta boundary; this revised report only includes allocations for dischargers within the legal Delta and the Yolo Bypass.
- Additional explanation of, and calculations for, the proposed methylmercury allocations to more directly address expected increases in source loading from predicted population growth and wetland restoration efforts.
- Changes to the methylmercury allocation strategy such that point and nonpoint sources with load-based allocations do not also have concentration allocations; this allows for a greater range of implementation options.
- Re-evaluation of the wetland and open-water methylmercury contributions (Chapter 6) using 2006 National Wetlands Inventory (NWI) wetland and open water acreages for the Delta/Yolo Bypass rather than the 1997 NWI acreages.
- Minor changes to methylmercury, total mercury and TSS load calculations (Chapters 6 and 7) based on additional quality assurance review of the concentration data and their use in regression-based load analyses.
- Minor textual changes throughout the report to clarify concepts and correct typographical errors identified in the June 2006 report.
- Expansion and re-location of the "Public Outreach" chapter (Chapter 9 in the June 2006 TMDL report) to the draft Basin Plan Amendment staff report (Chapter 8, "Public Participation & Agency Consultation").

Since the February 2008 draft TMDL Report issued for public review, staff made several more changes to the TMDL Report in response to comments made by stakeholders, as reflected in this January 2010 draft TMDL Report:

- Changes to the methylmercury allocation strategy so that NPDES facilities have more implementation options to address future population growth, regionalization, and reclamation.
- Minor modifications to methylmercury and total mercury load calculations (Chapters 6 and 7) based on (a) new inputs from NPDES facilities that previously did not discharge to surface water, (b) decreases because some NPDES facilities have ceased their discharges to surface water, (c) new discharge data for NPDES facilities for which previously no data were available; and (d) additional quality assurance review of the tributary inputs and NPDES facility concentration data and their use in load analyses.
- Addition of new information from recently completed CalFed mercury science reports and other recent published literature.
- Minor textual changes throughout the report to clarify concepts and correct typographical errors identified in the February 2008 report.

Staff reviewed key mercury studies in the Delta and elsewhere that have been published since the Delta methylmercury TMDL was drafted. These studies include the 2008 CALFED Bay Delta Program mercury studies and atmospheric deposition and wetland methylmercury loading research. Several of these studies are cited in Chapters 3, 6 and 7. Others have been discussed in stakeholder meetings. Staff concluded that recent information does not necessitate changes in the Delta TMDL at this time and generally supports a phased implementation strategy that includes development of methylmercury management measures, production of upstream TMDLs to address methylmercury and inorganic mercury sources, and methylmercury reductions for sources within the Delta. Staff will use studies published after the TMDL was developed to revise methylmercury and mercury load calculations and implementation strategy when the Delta methylmercury control program is reviewed at the end of Phase 1.

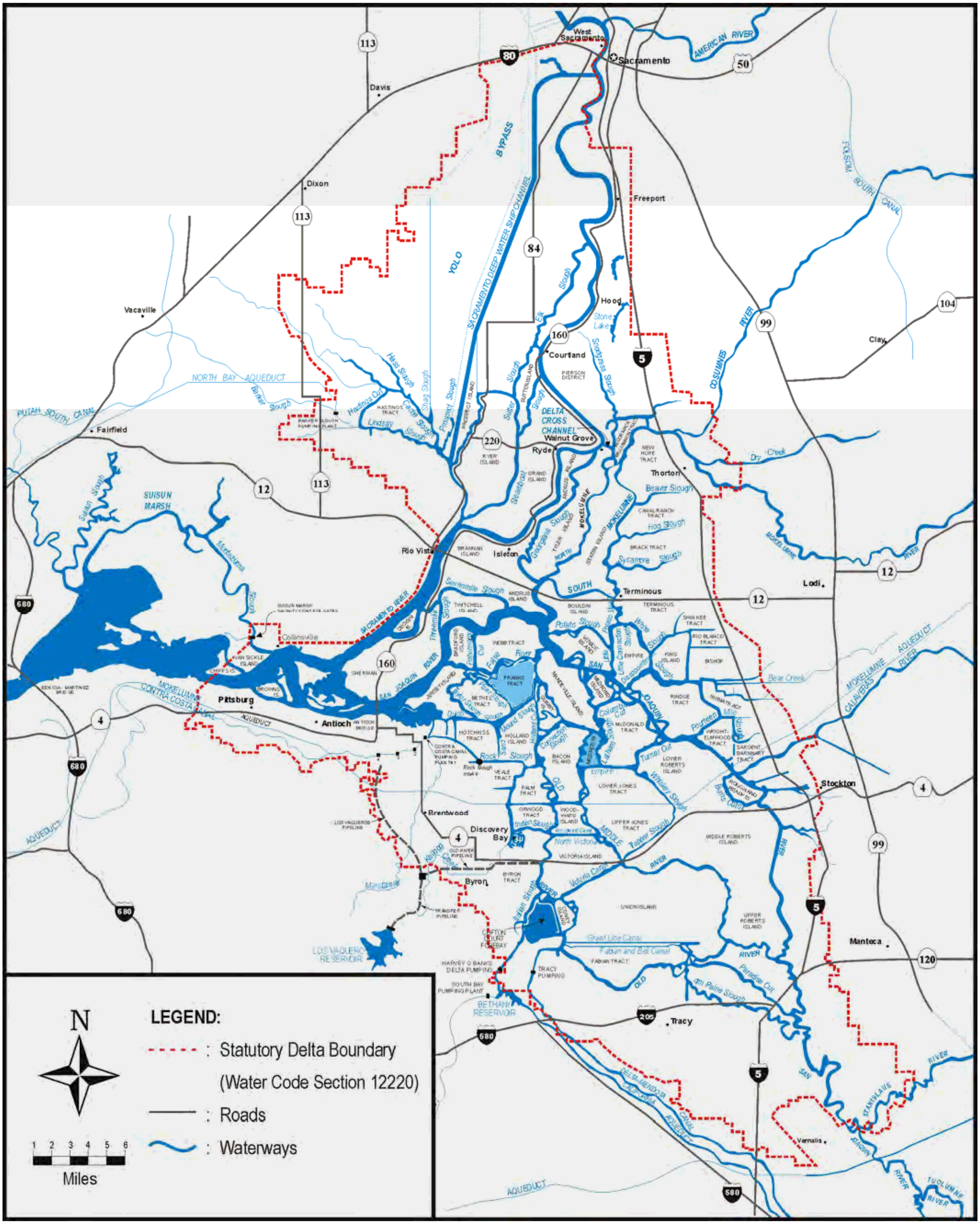

Figure 1.1: The Sacramento-San Joaquin Delta [DWR, 1995].
The dotted red line outlines the statutory boundary of the Delta.

2 PROBLEM STATEMENT

The Central Valley Water Board determined that the Delta is impaired by mercury. Fish-tissue data collected since 1970 in the Delta indicate that mercury levels exceed numeric criteria established for the protection of human and wildlife health. This Problem Statement presents information in four sections:

1. Regulatory Background and TMDL Timeline
2. Delta Characteristics and TMDL Scope
3. Mercury Effects & Sources
4. Beneficial Uses, Applicable Standards & Extent of Impairment

2.1 Regulatory Background & TMDL Timeline

2.1.1 Clean Water Act 303(d) Listing and Total Maximum Daily Load Development

Section 303(d) of the federal Clean Water Act requires states to:

- Identify waters not attaining water quality standards (referred to as the "303(d) list").
- Set priorities for addressing the identified pollution problems.
- Establish a "Total Maximum Daily Load" for each identified water body and pollutant to attain water quality standards.

In 1990 the State Water Resources Control Board (State Water Board) adopted the 303(d) List that identified Delta waterways as impaired for mercury because of the presence of a fish consumption advisory (SWRCB-DWQ, 1990). The 1998 303(d) List identified the TMDL control program for mercury in the Delta as a high priority (SWRCB-DWQ, 2003).

A TMDL represents the maximum load (usually expressed as a rate, such as kilograms per day (kg/day) or other appropriate measure) of a pollutant that a water body can receive and still meet water quality objectives. A TMDL describes the reductions needed to meet water quality objectives and allocates those reductions among the sources in the watershed. Water bodies on the 303(d) List are not expected to meet water quality objectives even if point source dischargers comply with their current discharge permit requirements. TMDLs must include the following elements: description of the problem (Chapter 2), numerical water quality target (Chapter 4), analysis of current loads (Chapters 6 and 7), and load reductions needed to eliminate impairments (Chapter 8).

2.1.2 Porter-Cologne Basin Plan Amendment Process

The State of California Porter-Cologne Water Quality Control Act (Section 13240) requires the Central Valley Water Board to develop a water quality control plan for each water body in the Central Valley that does not meet its designated beneficial uses. The Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (the Basin Plan) is the legal document that describes the beneficial uses of all water bodies in these basins, water quality objectives to protect them, and, if the objectives are not being met, an implementation program to correct the impairment (CVRWQCB, 1998). The water quality management strategy for mercury in the Delta includes:

- TMDL Development: involves the technical analysis of methyl and total mercury sources, fate and transport of each, development of proposed mercury fish tissue objectives, and a description of the amount of source reduction necessary to attain the proposed objectives.
- Basin Planning: focuses on the development of Basin Plan amendments and a staff report for Central Valley Water Board consideration. The draft Basin Plan amendments propose site-specific fish tissue objectives for the Delta and an implementation plan to achieve the objectives. The draft Basin Plan Amendment staff report includes information and analyses required to comply with the California Environmental Quality Act (CEQA). The Basin Planning process satisfies State Water Board regulations for the implementation of CEQA.[2]
- Implementation: focuses on the establishment of a framework that ensures that appropriate practices or technologies are implemented (§13241 and §13242 of the Porter-Cologne Water Quality Act), including those elements necessary to meet federal TMDL requirements (CWA Section 303(d)).

The proposed Basin Plan amendments are legally enforceable once they have been adopted by the Central Valley and State Water Boards and approved by the Office of Administrative Law and the USEPA. Central Valley Water Board staff solicited public participation and scientific review throughout the TMDL development and implementation planning phases. Chapter 8 in the draft Basin Plan Amendment staff report describes the extensive public participation, scientific peer review, and agency consultation that have taken place to date. Also, the Basin Plan amendments will be adopted and approved in a public forum.

2.1.3 Timeline and Process for the Delta Mercury Management Strategy

The Delta methylmercury TMDL and Basin Planning processes began with the development of a draft technical mercury TMDL report, which was submitted to the USEPA in August 2005 and posted on the Central Valley Water Board website for public review. The June 2006 TMDL Report incorporated additional information from ongoing sampling and analyses and public input received on the August 2005 draft TMDL report. The February 2008 draft TMDL report addressed scientific peer review comments and considered Central Valley Water Board member comments and questions voiced during the March 2007 workshop, additional input from agencies and other stakeholders, and supplementary evaluations to support the Basin Planning effort. This draft TMDL Report, along with the accompanying draft Basin Plan Amendment staff report and formal responses to comments under separate cover, addresses Central Valley Water Board member and stakeholder comments voiced during the April 2008 hearing and 2008-2009 Stakeholder Process. Chapter 8 in the draft Basin Plan Amendment

[2] The Secretary of Resources has certified the planning process for Basin Plans as a regulatory program pursuant to PRC § 21080.5 and CEQA Guidelines §15251(g). This certification means basin planning is exempt from CEQA provisions that relate to preparing Environmental Impact Reports and Negative Declarations. The Basin Plan Staff Report satisfies the requirements of State Board Regulations for Implementation of CEQA, Exempt Regulatory Programs, which are found in the California Code of Regulations, Title 23, Division 3, Chapter 27, Article 6, beginning with Section 3775.

staff report provides a detailed description of the CEQA scoping, Board, and public workshops and other stakeholder meetings that have taken place to date, including the formal Stakeholder Process. After staff has addressed any public comments on the draft TMDL and Basin Plan Amendment staff reports during the formal public review period, the final draft TMDL and Basin Plan Amendment staff reports will be presented to the Central Valley Water Board for their consideration later in 2010.

2.1.4 Units and Terms Used in this Report

This report uses the term “total mercury” (TotHg) to indicate the sum of all forms of mercury (Hg) in water: physical states (e.g., dissolved, colloidal or particulate bound), chemical states (e.g., elemental, mercurous ion, or mercuric ion), organic compounds (e.g., monomethylmercury), and inorganic compounds (e.g., cinnabar). Monomethylmercury is the predominant form of organic mercury present in biological systems and will be noted in this report as “methylmercury” (MeHg). Because methylmercury typically composes only a small portion of total mercury in ambient water,[3] the phrases “inorganic mercury” and “total mercury” are sometimes used synonymously.

Concentrations of methyl and total mercury in water (also referred to as “aqueous” methyl and total mercury) are reported in units of nanograms per liter (ng/l). Aqueous methylmercury concentrations are rounded to three decimal places and total mercury concentrations are rounded to two decimal places. Concentrations of suspended sediment are analyzed as total suspended solids (TSS) and use units of milligrams per liter (mg/l) rounded to one decimal place. In Chapter 7 (Source Assessment – Total Mercury & Suspended Sediment), the concentration of total mercury in suspended sediment is calculated as the ratio of concentrations of mercury to suspended sediments (TotHg:TSS). Units for the concentration of mercury in suspended sediment are part per million (ppm; equivalent to ng/mg or mg/kg), dry weight. Mercury levels in sediment and soil are also presented as part per million, dry weight. The units for loads of methylmercury and total mercury are grams per year (g/yr) and kilograms per year (kg/yr), respectively. Sediment loads are given in terms of millions of kilograms per year (kg/yr x 10^6 or Mkg/yr). Water flow is presented in units of acre-feet per year or million acre-feet per year (M acre-ft) for annual rates, cubic feet per second (cfs) for instantaneous flow measurements, and million gallons per day (mgd) for treatment plants. Load calculations are typically rounded to two significant figures with calculations completed prior to rounding. For this draft report, additional significant figures occasionally were included to improve the reader’s ease in verifying calculations.

Concentrations of mercury in fish tissue are reported as milligrams per kilogram (mg/kg), wet weight basis, rounded to two decimal places. Mercury is typically analyzed as “total mercury” in fish because of the additional cost required for methylmercury analysis. However, mercury exists almost entirely in the methylated form in small and top trophic level[4] fish (Nichols *et al*.,

[3] For example, a comparison of average annual methylmercury and total mercury loads from tributary watersheds to the Delta (Tables 6.2 and 7.1) indicates that methylmercury loading comprises only about 2% of all total mercury loading from the tributaries.

[4] Trophic levels are numerical descriptions of an aquatic food web. The USEPA’s 1997 Mercury Study Report to Congress used the following criteria to designate trophic levels based on an organism’s feeding habits:
Trophic level 1: Phytoplankton and bacteria.
Trophic level 2: Zooplankton, benthic invertebrates and some small fish.

1999; Becker and Bigham, 1995; Slotton *et al.*, 2004). Therefore, even though all the fish mercury data presented in the report were generated by laboratory analyses for total mercury, the data are described as “methylmercury concentrations in fish”.

Rates of fish consumption are given as grams of fish eaten per day (g/day) or meals per week. One adult human meal is assumed to be eight uncooked ounces (227 grams). Humans and wildlife species consume fish and other aquatic organisms from various size ranges and trophic levels. Safe fish tissue levels are identified in Chapter 4 for different trophic level and size classifications. These classifications are termed “trophic level food groups”.

For this report, methylmercury fish tissue concentrations in trophic level food groups are recommended as the TMDL water quality **targets**. The tissue targets will be proposed as options for the Central Valley Water Board to consider when adopting fish tissue objectives. The term **implementation goal** in this report refers to methylmercury concentrations in standard 350-mm largemouth bass and unfiltered water, which are correlated to the targets. The implementation goal for methylmercury in unfiltered ambient water is Central Valley Water Board staff’s best estimate of the annual average methylmercury concentration in water needed to achieve the fish tissue targets. The “implementation goal” for methylmercury in ambient water is used to determine the methylmercury source load reductions necessary to meet the targets. The water and largemouth bass methylmercury goals are not being proposed as water quality objectives.

2.2 Delta Characteristics and TMDL Scope

2.2.1 Delta Geography

The Sacramento-San Joaquin Delta, along with the San Francisco Bay, forms the largest estuary on the west coast of North America. The Delta encompasses a maze of over 1,100 miles of river channels surrounding about 738,000 acres (1,153 square miles) of diked islands and tracts in Alameda, Contra Costa, Sacramento, San Joaquin, Solano and Yolo counties (Figure 1.1 and Figure A.1 in Appendix A). Many of the Delta waterways follow natural courses while others have been constructed to provide deep-water navigation channels, to improve water circulation, or to obtain material for levee construction (DWR, 1995). The legal boundary of the Delta is defined in California Water Code Section 12220. Appendix A illustrates the more than 100 named waterways addressed by this TMDL.

The Delta and its source watersheds comprise nearly 40% of the landmass of the State of California (Table 2.1 and Figure 2.1). The Sacramento, San Joaquin, Mokelumne, Cosumnes, and Calaveras rivers all flow into the Delta, carrying approximately 47% of the State’s total runoff (DWR, 2005). Major reservoirs and lakes in the Sacramento Basin include Shasta, Whiskeytown, Oroville, Englebright, Camp Far West, Folsom, and Black Butte, Indian Valley, Clear Lake and Lake Berryessa. Major reservoirs and lakes in the San Joaquin Basin include Camanche, New Hogan, New Melones/Tulloch, Don Pedro, McClure, Burns, Bear, Owens, Eastman, Hensley, Millerton and Marsh Creek.

Trophic level 3: Organisms that consume zooplankton, benthic invertebrates, and other TL2 organisms.
Trophic level 4: Organisms that consume TL3 organisms.

The legal Delta encompasses the southern two thirds of the Yolo Bypass, a 73,300-acre floodplain on the west side of the lower Sacramento River. The Fremont and Sacramento Weirs route floodwaters from the Sacramento River and its associated tributary watersheds around the Sacramento urban area to the Yolo Bypass. Cache and Putah Creeks, Willow Slough, and the Knights Landing Ridge Cut from the Colusa Basin all drain directly to the Yolo Bypass.

The Sacramento River contributes an average annual water volume of 18.3 million acre-feet and the Yolo Bypass and the San Joaquin River contribute an average of 5.8 million acre-feet. Diversions in the Delta include the State Water Project (Banks Pumping Plant and the North Bay Aqueduct), Central Valley Project (Tracy Pumping Plant), and Contra Costa Water District, which withdraw average annual water volumes of about 3.7 million, 2.5 million, and 126 thousand acre-feet, respectively (DWR, 2005). During a typical water year,[5] the Delta receives runoff only from the Sacramento and San Joaquin Basins in the Central Valley (Figure 2.1). During infrequent flood events, the Tulare Basin in the southern Central Valley is connected to the San Joaquin River system.

The mean annual precipitation in the City of Stockton in the eastern Delta is approximately 14 inches, with the majority of rain falling between November and March. Temperatures at Stockton typically average 62 degrees Fahrenheit (^{o}F), with summer highs exceeding 90 ^{o}F and winter lows dropping below 40 ^{o}F.

The Delta had a population of 410,000 people in 1990 (DWR, 1995). As of the 2000 Census, about 462,000 people resided in the Delta region (DWR, 2005). Rapid growth is occurring in urban areas in and surrounding the Delta, especially in Elk Grove (27% growth per year – the highest growth rate in California), Tracy (5.9% per year), Brentwood (12.3% per year), and Rio Vista (11.1% per year).

Agriculture and recreation are the two primary businesses in the Delta. The Delta also provides habitat for over five hundred species of wildlife (DWR, 1995; Herbold *et al.*, 1992). The Delta is the major source of fresh water to San Francisco Bay and supplies drinking water for over two-thirds of the State's population (over 23 million people) and irrigation water for more than seven million acres of farmland statewide (DWR, 2005). Table 2.2 lists additional features of the Delta.

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5 A "water year" (WY) is defined as the period between 1 October and 30 September of the following year; for example, WY2001 is the period between 1 October 2000 and 30 September 2001. Water year types in California are classified according to the natural water production of the major basins. See Appendix E for more information about water year classifications.

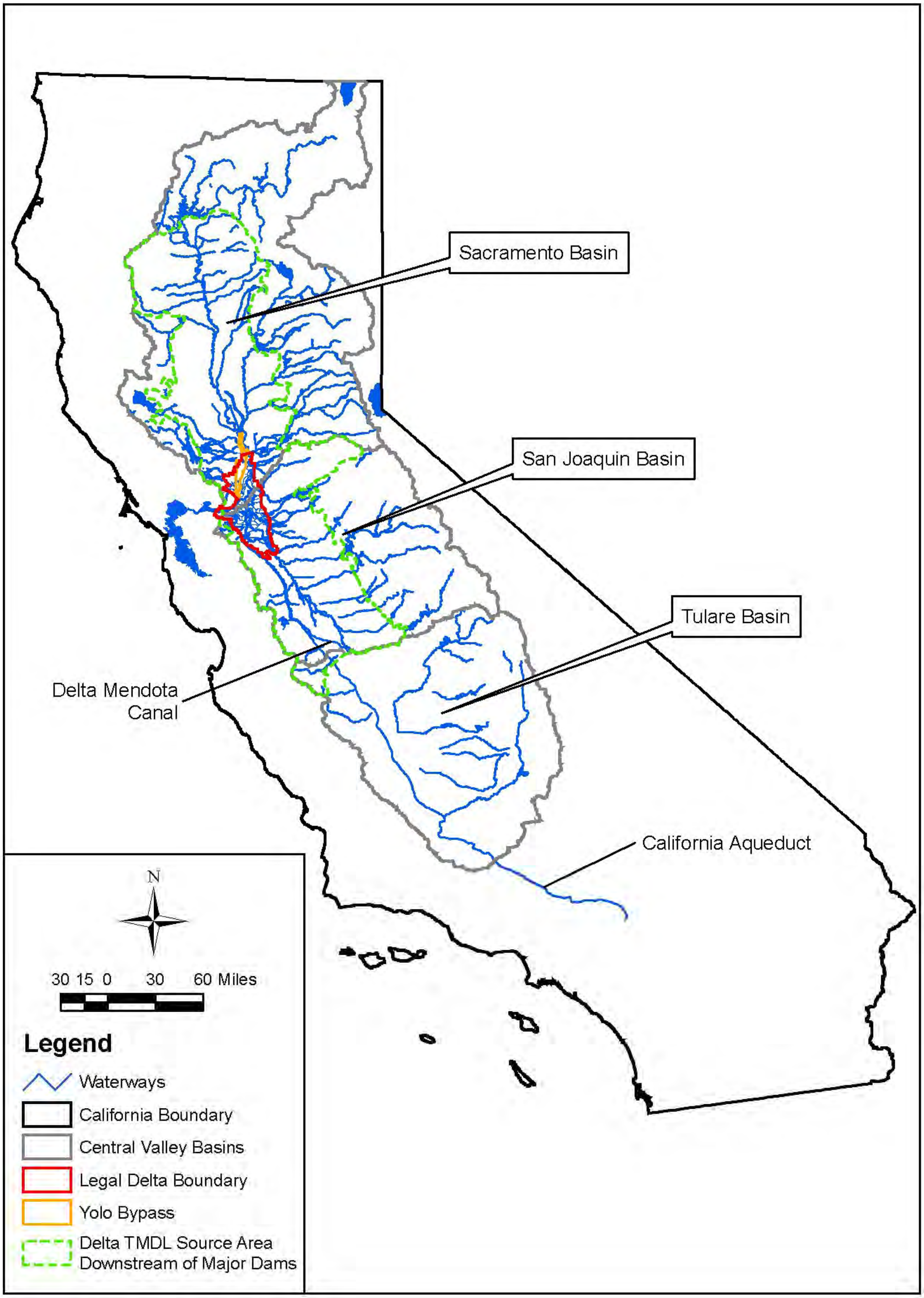

Figure 2.1: The Central Valley

Table 2.1: Spatial Perspective of the Delta and Its Source Regions

Region	Acreage	Square Miles	% of California	% of Central Valley
California	101,445,246	158,508	---	---
Central Valley	37,982,554	59,348	37%	---
Delta (legal boundary)	737,630	1,153	1%	1.9%
Delta Watershed (Statutory Delta & all tributary watersheds that ultimately drain directly to the Delta)	27,226,796	42,542	27%	72%
Delta Watershed Area Downstream of Major Dams	12,469,054	19,483	12%	33%
Sacramento River Watershed	17,410,314	27,204	17%	46%
San Joaquin River Watershed	9,801,103	15,314	10%	26%

Table 2.2: Key Delta Features (DWR, 1995 and 2005)

Population:	410,000 (1990), 462,000 (2000)	Area (acres):	Agriculture: 538,000 Cities & towns: 64,000 Water surface: 61,000 Undeveloped: 75,000 *Total: 738,000*
Incorporated cities entirely within the Delta:	Antioch, Brentwood, Isleton, Pittsburg, Tracy		
Major cities partly within the Delta:	Sacramento, Stockton, West Sacramento		
# of unincorporated towns and villages:	14	Total length of all leveed channels:	1,100 miles (1987)
Main crops:	Alfalfa asparagus corn fruit grain & hay grapes pasture safflower sugar beets tomatoes	Diversions from the Delta:	Central Valley Project State Water Project Contra Costa Canal City of Vallejo Western Delta Industry 1,800+ Agricultural diversions
		Rivers flowing into the Delta:	Calaveras Cosumnes Sacramento San Joaquin Mokelumne

Fish and wildlife:	# of Species [(a)]	# of Federal & State Species of Concern [(a)]	# of Non-Native Species [(b)]
Birds:	230	10	3
Mammals:	45	9	7
Fish:	52	8	30
Reptiles & amphibians:	25	6	1
Flowering plants:	150	54	70
Invertebrates:	na	21	13

Major anadromous fish: American shad, salmon, steelhead trout, striped bass, sturgeon

(a) Endangered, threatened, rare, and candidate species per the federal listing effective January 31, 1992, and the state listing effective April 9, 1992, as cited in the Sacramento – San Joaquin Delta Atlas (DWR, 1995).

(b) Introduced species in the Sacramento – San Joaquin Delta, as cited in the Sacramento – San Joaquin Delta Atlas (DWR, 1995).

2.2.2 TMDL Scope & Delta Subareas

This TMDL addresses fish mercury impairment in all waterways within the legal Delta, except the westernmost portion of the Delta near Chipps Island that falls within the jurisdiction of the San Francisco Bay Regional Water Quality Control Board (Figure 2.2; see Appendix A for a list of named waterways). Tributaries are considered to be nonpoint sources to the Delta and are evaluated at or near the locations where they cross the statutory Delta boundary. Assessment of point and nonpoint sources that contribute to tributary discharges to the Delta is ongoing and will be described in reports for future mercury TMDL programs for those watersheds and implementation activities for the Delta methylmercury TMDL.

The methylmercury source analysis and linkage analysis for the Delta TMDL divide the Delta into eight regions based on the hydrologic characteristics and mixing of the source waters (Figure 2.2) (e.g., DWR, 1991 and 1962). A hydrology-based methylmercury TMDL is proposed in this report as it more accurately reflects the concentrations and sources of methylmercury and the extent of fish impairment. As described in Chapter 8 (Allocations), essentially a separate methylmercury allocation scheme is developed for each subarea because the methylmercury sources and level of fish impairment in each subarea are different. The following paragraphs describe the delineation of the hydrologic subareas. These subareas are different from the Delta water body segment delineation ("portions") defined by the State Water Board for the 2006 Clean Water Act Section 303(d) List (SWRCB-DWQ, 2006).

<u>Sacramento River</u>: This subarea is dominated by Sacramento River flows. It is bound to the east by the legal Delta boundary and to the west by the eastern levee of the Sacramento Deep Water Ship Channel. Sacramento River flows influence the Upper and Lower Mokelumne River in the Delta because of diversions by the Delta Cross Channel near Walnut Grove (Figure A.1 in Appendix A). The Delta Cross Channel controls diversions of fresh water from the Sacramento River to Snodgrass Slough and the Mokelumne River to combat salt-water intrusion in the Delta, to dilute local pollution, and to more efficiently supply the federal Central Valley Project and State Water Project pumps in the southern Delta.

Although drawn as a line, the Sacramento River subarea's boundary with the South Yolo Bypass, Central Delta, and West Delta subareas is defined by a gradient in water quality characteristics that varies with the tidal cycle, magnitude of wet weather flows, diversions by within-Delta control structures, and releases from reservoirs in the upstream watersheds.

<u>Yolo Bypass - North & South</u>: The Yolo Bypass is a 73,300-acre floodplain on the west side of the lower Sacramento River (see Section E.2.2 and Figure E.2 in Appendix E for the floodplain boundary definition). The Fremont and Sacramento Weirs route floodwaters to the Yolo Bypass from the Sacramento and Feather Rivers and their associated tributary watersheds. Cache and Putah Creeks, Willow Slough, and the Knights Landing Ridge Cut from the Colusa Basin all drain directly to the Yolo Bypass. The legal Delta encompasses only the southern two thirds of the Yolo Bypass. The "Yolo Bypass – North" subarea is defined by Fremont Weir to the north and Lisbon Weir to the south and includes areas within and north of the legal Delta boundary. The "Yolo Bypass – South" subarea is defined by Lisbon Weir to the north and the southern end of Cache Slough to the south. Lisbon Weir (Figure E.2) limits the range of tidal fluctuation upstream in the Yolo Bypass.

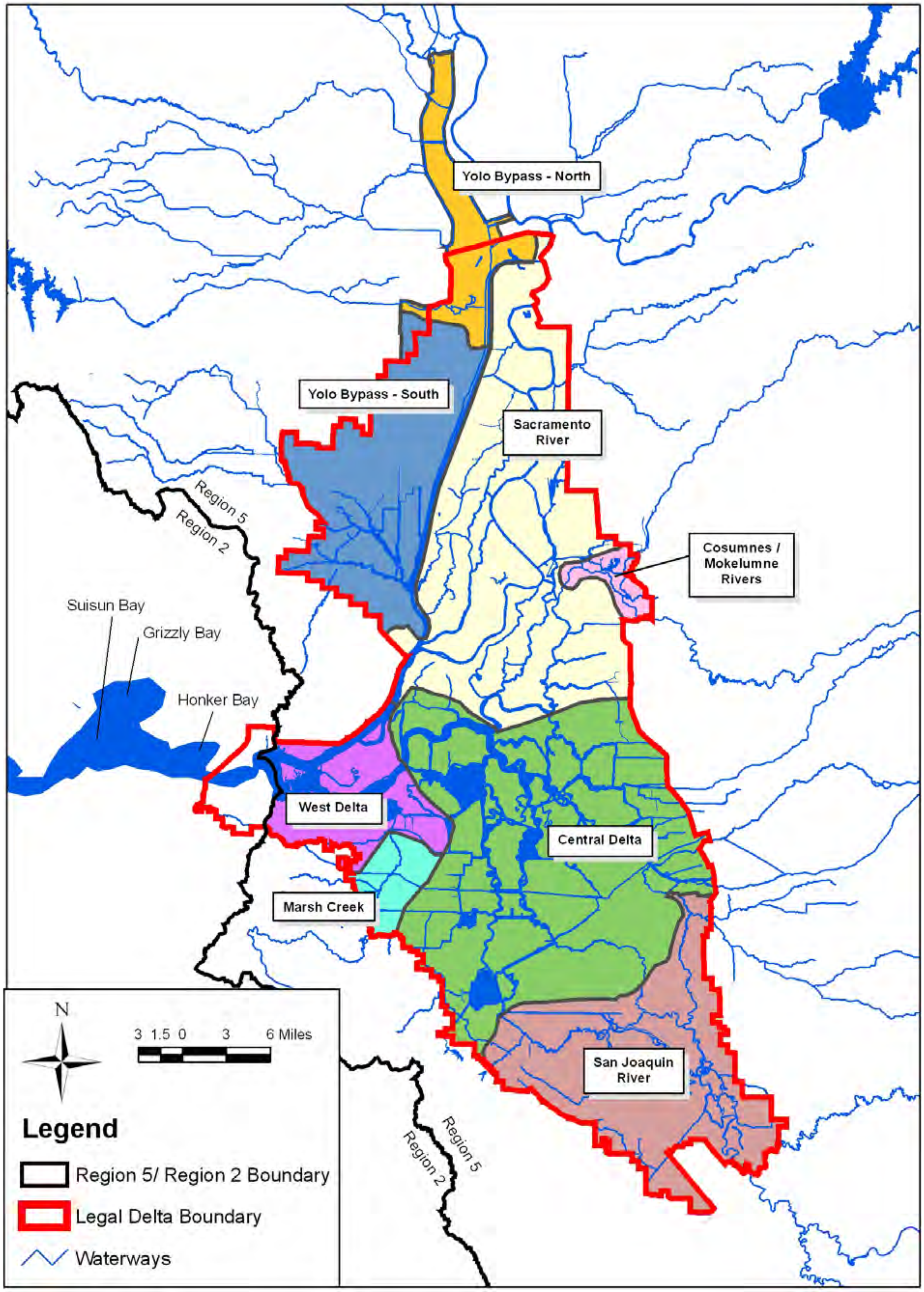

Figure 2.2: Hydrology-Based Delineation of Subareas within the Legal Delta and Yolo Bypass

Cosumnes/Mokelumne Rivers: This subarea includes the lower Cosumnes and Mokelumne Rivers and is defined by the legal Delta boundary to the east and the Delta Cross Channel confluence with the Mokelumne to the west.

San Joaquin River: This subarea is defined by the legal Delta boundary to the east and south, and Grantline Canal and the beginning of the Stockton Deep Water Channel to the north. At present, the San Joaquin River is almost entirely diverted out of the Delta by way of Old River and Grantline Canal for export south of the Delta via the state and federal pumping facilities near Tracy.

Marsh Creek: This subarea is defined by the portion of the Marsh Creek watershed within the legal Delta boundary that is upstream of tidal effects.

West Delta: The West Delta subarea encompasses the confluence of the Sacramento and San Joaquin Rivers, which transport water from the Central Valley to the San Francisco Bay. The western border of the West Delta subarea is defined by the jurisdictional boundary between the Central Valley Regional Water Quality Control Board (Region 5) and the San Francisco Water Board (Region 2) (Figure 2.2). Water quality characteristics are determined by the tidal cycle, magnitude of wet weather flows, controlled flow diversions by within-Delta structures, and releases from reservoirs in the upstream watersheds.

Central Delta: The Central Delta includes a myriad of natural and constructed channels that transport water from the upper watersheds to San Francisco Bay to the west and the state and federal pumps to the southwest. The Central Delta tends to be most influenced by waters from the Sacramento River.

2.3 Mercury Effects & Sources

2.3.1 Mercury Chemistry and Accumulation in Biota

Mercury (Hg) can exist in various forms in the environment. Physically, mercury can exist in water in a dissolved, colloidal or particulate bound state. Chemically, mercury can exist in three oxidation states: elemental (Hg^{0}), mercurous ion (monovalent, Hg^{+}), or mercuric ion (divalent, Hg^{+2}). Ionic mercury can react with other chemicals to form both organic and inorganic compounds, such as cinnabar (HgS), and can be converted by sulfate reducing bacteria to more toxic organic compounds, such as monomethylmercury (CH_3Hg) or dimethylmercury ($(CH_3)_2Hg$). Important factors controlling the conversion rate of inorganic to organic mercury include temperature, percent organic matter, redox potential, salinity, pH, and mercury concentration. Monomethylmercury is the predominant form of organic mercury present in biological systems and will be noted in this report as methylmercury or “MeHg”. Because dimethylmercury is an unstable compound that dissociates to monomethylmercury at neutral or acid pH, it is not a concern in freshwater systems (USEPA, 1997a). Chapter 3 provides more information about potentially controllable methylation processes in the Delta region.

Both inorganic and organic mercury can be taken up by aquatic organisms from water, sediments and food. Low trophic level species such as phytoplankton obtain all their mercury directly from the water. *Bioconcentration* describes the net accumulation of mercury directly from water. The *bioconcentration factor* is the ratio of mercury concentration in an organism to mercury concentration in water. Mercury may also accumulate in aquatic organisms from consumption of mercury-contaminated prey (USEPA, 1997b). Mercury *bioaccumulates* in organisms when rates of uptake are greater than rates of elimination.

Repeated consumption and accumulation of mercury from contaminated food sources results in tissue concentrations of mercury that are higher in each successive level of the food chain. This process is termed *biomagnification*. Methylmercury accumulates within organisms more than inorganic mercury because inorganic mercury is less well absorbed and/or more readily eliminated than methylmercury. The proportion of mercury that exists as the methylated form generally increases with the level of the food chain. Methylmercury comprises 85% to 100% of the total mercury measured in fish (Becker and Bigham, 1995; Nichols *et al.*, 1999; Slotton *et al.*, 2004).

Consumption of contaminated, high trophic level fish is the primary route of methylmercury exposure. For example, the aquatic food web provides more than 95% of humans' intake of methylmercury (USEPA, 1997a). Wildlife species of potential concern that consume fish and other aquatic organisms from the Delta include piscivorous fish, herons, egrets, mergansers, grebes, bald eagle, kingfisher, peregrine falcon, osprey, mink, raccoon and river otter.

2.3.2 Toxicity of Mercury

Mercury is a potent neurotoxicant. Methylmercury is the most toxic form of this metal. Methylmercury exposure causes multiple effects, including tingling or loss of tactile sensation, loss of muscle control, blindness, paralysis, birth defects and death. Adverse neurological effects in children appear at dose levels five to ten times lower than associated with toxicity in adults (NRC, 2000). Children may be exposed to methylmercury during fetal development, by eating fish, or through both modes. Effects of methylmercury are dose dependent.

Wildlife species may also experience neurological, reproductive or other detrimental effects from mercury exposure. Behavioral effects such as impaired learning, reduced social behavior and impaired physical abilities have been observed in mice, otter, mink and macaques exposed to methylmercury (Wolfe *et al.*, 1998). Reproductive impairment following mercury exposure has been observed in multiple species, including common loons and western grebe (Wolfe *et al.*, 1998), walleye (Whitney, 1991 in Huber, 1997), mink (Dansereau *et al.*, 1999) and fish (Huber, 1997; Wiener and Spry, 1996).

2.3.3 Mercury Sources & Historic Mining Activities

Identified sources of methyl and total mercury in the Delta and in tributary watersheds include geothermal springs, methylmercury flux from sediments in wetlands and open water habitats, municipal and industrial dischargers, agricultural drainage, urban runoff, atmospheric deposition, and erosion of naturally mercury-enriched soils and excavated overburden and tailings from historic mining operations. Although none are present within the legal Delta, historic mercury and gold mining sites – along with their associated contaminated waterways – may contribute a substantial portion of the total mercury in the tributary discharges to the Delta.

Chapters 6 and 7 provide a detailed assessment of the within-Delta sources of methyl and total mercury.

As noted in source analyses in Chapters 6 and 7, tributary inputs to the Delta are the largest sources of methyl and total mercury. These tributaries drain many of the major mercury mining districts in the Coast Range and the placer gold mining fields in the Sierra Nevada Mountains. The Coast Range is a region naturally enriched in mercury. Active geothermal vents and hot springs deposit mercury, sulfur, and other minerals at or near the earth's surface. Most of the mercury deposits in California occur within a portion of the Coast Range geomorphic province extending from Clear Lake in Lake County in the north to Santa Barbara County in the south. Approximately 90% of the mercury (roughly 104 million kilograms) used in the United States between 1846 and 1980 was mined in the Coast Range of California (Churchill, 2000). Much of the mining and extraction occurred prior to 1890 when mercury processing was crude and inefficient. The ore was processed at the mine sites, with about 35 million kilograms of mercury lost at the mine sites. As a result, high levels of mercury are present in sediment and fish tissue in Coast Range water bodies. Fish advisories have been posted for Clear Lake, Cache Creek, Lake Berryessa and Black Butte Reservoir (Stratton *et al.*, 1987; Brodberg and Klasing, 2003; Gassel *et al*., 2005). Mercury mine waste enters the Delta from mine-impacted Coast Range creeks such as Cache, Putah and Marsh Creeks.

Approximately 10 million kilograms of Coast Range mercury were transported across the valley and used as an amalgam in placer and lode gold mining in the Sierra Nevada Mountains between 1850 and 1890 (Churchill, 2000). Approximately six million kilograms of mercury were lost in Sierra Nevada rivers and streams during gold mining operations. Principal gold mining areas were in the Yuba River and Bear River (tributaries to the Sacramento River via the Feather River), the Cosumnes River (a tributary to the Mokelumne River), and the Stanislaus, Tuolumne and Merced Rivers (tributaries to the San Joaquin River). Elevated mercury concentrations are present in fish in all these Sierra Nevada waterways. Floured[6] elemental mercury enters the Delta from the Sacramento, Mokelumne and San Joaquin Rivers.

Evaluation of legacy mine sites, associated contaminated waterway reaches, and other methyl and total mercury sources that contribute to tributary inputs to the Delta is ongoing. More detailed source analyses for the tributary watersheds will be conducted by future mercury TMDL programs for those watersheds and by proposed implementation actions for the Delta mercury control program (see Chapter 4 in the draft Basin Plan Amendment staff report).

[6] Flouring is the division of mercury into extremely small globules, which gives it a white, flour-like appearance. If the floured mercury has surface impurities such as oil, grease, clay or iron and base metal sulfides, it will not coalesce into larger drops or form an amalgam with gold (Beard, 1987). Mercury was used for gold recovery throughout the Sierra Nevada. Floured mercury was formed by the pounding of boulders and gravels over liquid mercury in hydraulic mining-related sluice boxes (Hunerlach *et al.*, 1999), as well by intense grinding in the hardrock milling systems, and was transported downstream with tailings.

2.4 Beneficial Uses, Applicable Standards & Extent of Impairment

2.4.1 Sacramento-San Joaquin Delta Estuary Beneficial Uses

The federal Clean Water Act and the State Water Code (Porter-Cologne Water Quality Act) require the State to identify and protect the beneficial uses of its waters. Table 2.3 lists the existing beneficial uses of the Delta. Human consumption of fish and shellfish (currently assumed under REC-1) and wildlife habitat (WILD) are impaired because of elevated mercury concentrations in fish throughout the Delta. The Basin Plan does not include a commercial and sport fishing (COMM) designation for the Delta, which includes uses of water for commercial or recreational collection of fish, shellfish, or other organisms intended for human consumption or bait purposes. However, as described in Appendix C, commercial and sport fishing take place in the Delta. Some sport and commercial species (e.g., striped bass and largemouth bass) are impaired by mercury, while others (e.g., salmon and clams) are not. The draft Basin Plan Amendment staff report considers adoption of a COMM beneficial use for the Delta.

The municipal and industrial supply (MUN) beneficial use is designated in the Basin Plan for all waterways within the legal Delta boundary except Marsh Creek and Yolo Bypass (e.g., Cache Creek Settling Basin outflow, Prospect Slough, and the downstream segment of Putah Creek within the Yolo Bypass). Staff evaluated whether levels of total mercury in water in Delta waterways support the MUN beneficial use. The California Toxics Rule (CTR) criterion for mercury protects humans from exposure to mercury through fish consumption and drinking water and is enforceable for all waters with a municipal and domestic water supply or aquatic beneficial use designation. As described in Sections 2.4.2 and 7.4.2, the CTR mercury criterion is exceeded in outflow from the Cache Creek Settling Basin and possibly in Prospect Slough, Putah Creek, and Marsh Creek; however, MUN is not designated for these waterways. Mercury reductions may be needed to meet the CTR in the Yolo Bypass downstream of the Cache Creek Settling Basin and in Marsh Creek, but these reductions will be addressed by the existing TMDL for Cache Creek and future TMDLs for the Marsh Creek and Putah Creek watersheds (see Section 7.4.2), in addition to actions designed to reduce fish methylmercury concentrations in the Delta/Yolo Bypass and total mercury exports to San Francisco Bay (see Section 8.2).

Table 2.3: Beneficial Uses of the Delta and Yolo Bypass [a]

Beneficial Use	Delta Status	Yolo Bypass Status
Municipal and domestic supply (MUN)	Existing [b]	
Agriculture – irrigation and stock watering (AGR)	Existing	Existing
Industry – process (PROC) and service supply (IND)	Existing	
Contact recreation (REC-1) [c]	Existing [b]	Existing [b]
Non-contact recreation (REC-2) [c]	Existing	Existing
Freshwater habitat (warm water species)	Existing	Existing
Freshwater habitat (cold water species)	Existing	Potential
Spawning, reproduction and/or early development of fish (SPWN) (warm water species)	Existing	Existing
Wildlife habitat (WILD)	Existing [b]	Existing [b]
Migration of aquatic organisms (MIGR) (warm and cold water species)	Existing	Existing
Navigation (NAV)	Existing	

(a) This table lists the beneficial uses designated for the Delta and Yolo Bypass in Table II-1 of the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (Basin Plan) (CVRWQCB, 2007). The Yolo Bypass is a 73,300-acre floodplain on the west side of the lower Sacramento River. The lower two thirds of the Yolo Bypass are within the legal Delta, and waterways within the entire Delta are included in Clean Water Act 303(d) List. However, Table II 1 of the Basin Plan includes separate table rows for the Yolo Bypass and Delta.

(b) These are beneficial uses impaired by mercury in the Delta, including portions of the Yolo Bypass within the legal Delta boundary.

(c) REC-1 includes recreational activities involving body contact with water, where ingestion of water is reasonably possible. These uses include, but are not limited to, swimming, wading, water-skiing and fishing. REC-2 includes recreational activities involving proximity to water, but where there is generally no body contact with water, nor any likelihood of ingestion of water. These uses include, but are not limited to, picnicking, sunbathing, hiking, beachcombing, camping, boating, hunting and sightseeing.

2.4.2 Applicable Standards & Extent of Impairment

The narrative water quality objective for toxicity in the Basin Plan states, “All waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life.” The narrative toxicity objective further says that “The Regional Water Board will also consider … numerical criteria and guidelines for toxic substances developed by the State Water Board, the California Office of Environmental Health Hazard Assessment, the California Department of Health Services, the U.S. Food and Drug Administration, the National Academy of Sciences, the USEPA, and other appropriate organizations to evaluate compliance with this objective” (CVRWQCB, 1998). Four potential criteria were evaluated to determine whether the Delta was in compliance with the narrative objective. They are the USEPA and USFWS fish tissue criteria for protection of human and wildlife, the USEPA aqueous methylmercury criterion for drinking water, the United Nations aqueous total mercury guidance level to protect livestock, and the California Toxic Rule (CTR) aqueous total mercury criterion for protection of human and wildlife health. Each is reviewed below and a determination made as to whether the recommended criteria or objective is met in the Delta.

2.4.2.1 *Fish Tissue Criteria*

In 1971, a human health advisory was issued for the Sacramento-San Joaquin Delta advising pregnant women and children not to consume striped bass. In 1994, an interim advisory was issued by the California Office of Environmental Health Hazard Assessment (OEHHA) for San Francisco Bay and Delta recommending no consumption of large striped bass and shark because of elevated concentrations of mercury and polychlorinated biphenyls (OEHHA, 1994). Additional monitoring indicates that several more species, including largemouth bass and white catfish (two commonly-caught local sport fish), also have elevated concentrations of mercury in their tissue (Davis *et al.*, 2003; Slotton *et al.*, 2003; LWA, 2003; SWRCB-DWQ, 2002).

In 2007, OEHHA issued drafts of safe eating guidelines for the South Delta and the lower Cosumnes River, lower Mokelumne River, and San Joaquin River from Port of Stockton to Friant Dam[7] (OEHHA, 2006 and 2007). The South Delta guidelines encompass much of the Central Delta, West Delta, and San Joaquin River subareas of the TMDL. All of the new guidelines continue restrictions on consumption of striped bass. In addition, the new guidelines provide consumption advice for other sport fish, crayfish, and clams. OEHHA suggests that pregnant and nursing women should limit consumption of largemouth bass, carp, and crappie to 8 ounces uncooked fish per week in the South Delta and should avoid largemouth bass from the San Joaquin and lower Cosumnes Rivers. OEHHA anticipates releasing safe eating guidelines in 2008 for the North Delta, which would cover the Sacramento River and rest of the Central Delta TMDL subareas.

The Delta was listed for mercury because of the 1971 and 1994 fish advisories and because some fish tissue concentrations exceeded the National Academy of Sciences (NAS) guidelines for protection of wildlife health. The NAS wildlife guideline is 0.5 mg/kg mercury in whole, freshwater fish (NAS, 1973). The USEPA has since published a recommended criterion for the protection of human health of 0.3 mg/kg mercury in fish tissue (USEPA, 2001). Similarly, the USFWS has provided guidance on safe methylmercury ingestion rates for sensitive wildlife species (USFWS, 2002, 2003 and 2004). The Delta TMDL cites the USEPA and USFWS recommended criteria for protection of human and wildlife health, as these are more protective.

Significant regional variations in fish tissue mercury concentrations are observed in the Delta. Elevated concentrations occur along the periphery of the Delta while lower body burdens are measured in the central Delta. A summary of fish tissue methylmercury concentrations by Delta subarea is provided in Chapter 4 (Tables 4.7 and 4.10) and Appendix C. Concentrations are greater than recommended as safe by the USEPA and USFWS at all locations except in the central Delta. Percent reductions in fish methylmercury levels ranging from 0% to 80% in the peripheral Delta subareas will be needed to meet the numeric targets for wildlife and human health protection.

2.4.2.2 *Aqueous Criteria & Guidance*

The USEPA recommends a safe level of 70 ng/l methylmercury in drinking water to protect humans (USEPA, 1987). This level was released through USEPA's Integrated Risk Information

[7] OEHHA's recent advisories are in the form of safe eating guidelines that indicate which fish species may be eaten safely as well as those that should be avoided or eaten less frequently.

System (IRIS) and was based on USEPA's recommended methylmercury reference dose for lifetime exposure. Methylmercury concentrations in the Delta typically range from 0.02 to 0.3 ng/l (Section 6.2.1). The maximum observed concentration in the Delta between March 2000 and April 2004 was 0.70 ng/l in Prospect Slough in March 2000 (Appendix L). The USEPA IRIS drinking water criterion is not expected to be exceeded in the Delta.

The United Nations recommends a guidance level of 10,000 ng/l unfiltered total mercury to protect livestock drinking water (Ayers and Westcot, 1985). Unfiltered mercury concentrations in the Delta typically range from 0.26 to 100 ng/l (Table 7.4 in Chapter 7). The maximum concentration ever observed in the Delta was 696 ng/l at Prospect Slough on January 10, 1995. The United Nations recommended livestock guidance level is not expected to be exceeded in the Delta.

The USEPA promulgated the CTR in April 2000 (USEPA, 2000b). The CTR mercury criterion is 0.05 µg/L (50 ng/l) total recoverable mercury for freshwater sources of drinking water. The CTR criterion was developed to protect humans from exposure to mercury in drinking water and in contaminated fish. It is enforceable for all waters with beneficial use designations of municipal and domestic water supply. This includes all subareas of the Delta except Yolo Bypass and Marsh Creek. As indicated earlier in Table 2.3, Basin Plan Table II-1 does not designate "MUN" for the Yolo Bypass and Marsh Creek; however, it does designate recreation (including fish consumption by humans). The CTR does not specify duration or frequency. The Central Valley Water Board has previously employed a 30-day-averaging period with an allowable exceedance frequency of once every three years.[8]

An evaluation of unfiltered total mercury concentrations demonstrates that the CTR mercury criterion is not exceeded anywhere in the Delta. Mercury concentrations are greater than the CTR criterion downstream of the Cache Creek Settling Basin in the Yolo Bypass and possibly in Putah Creek outflow to Yolo Bypass, Prospect Slough and Marsh Creek (Section 7.4.2). These water bodies are not designated for MUN. The mercury concentrations greater than the CTR criterion downstream of Cache Creek may be addressed by the Cache Creek mercury control program (Cooke and Morris, 2005) adopted in October 2005 and proposed upgrades of the Cache Creek Settling Basin described in Chapter 4 of the draft Basin Plan Amendment staff report. Prospect Slough is downstream of Cache Creek and potential exceedances of the CTR could be corrected with decreases in mercury loads from Cache Creek and its settling basin. Putah and Marsh Creeks are both on the 303(d) list because of elevated mercury concentrations. Potential exceedance of the CTR downstream of these water bodies will be addressed by load reductions to be determined by their TMDLs. Chapters 7 and 8 will provide additional evaluations of total mercury loads from these watersheds and potential reduction strategies.

Regardless of whether MUN is specifically designated by the Basin Plan (and the CTR criterion is enforceable), the numeric targets and mercury control actions in this and other TMDLs will ensure that the CTR's level of human health protection is met throughout the Delta and Yolo Bypass. The CTR mercury criterion protects human health and is intended to be used where consumption of aquatic organisms occurs, which includes the Delta with the Marsh Creek

[8] Personal communication from P. Woods (USEPA Region 9) to J. Marshack (CVRWQCB), 4 December 2001.

subarea and Yolo Bypass. The proposed fish tissue objective will also apply to all of the Delta subareas and the Yolo Bypass. Since the proposed fish tissue objectives are more stringent than the CTR mercury criterion, attainment of the fish tissue objectives will also meet the aim of the CTR for protection of people that eat local fish.

The USFWS and the U.S. National Marine Fisheries Service are concerned that the mercury objective in the CTR may not protect threatened and endangered species and requested that the USEPA reevaluate the criterion. The USEPA has not released a reevaluation. Staff developed the TMDL's wildlife target evaluation and the Basin Plan amendments' proposed fish tissue objective for small fish with guidance from USFWS to ensure that threatened and endangered species will be protected.

2.4.2.3 San Francisco Bay Mercury TMDL's Allocation for Total Mercury in Central Valley Outflows

As a component of the mercury control program for the San Francisco Bay, San Francisco Water Board staff developed a target for San Francisco Bay sediment mercury concentration (particle-bound mercury mass divided by sediment mass) of 0.2 mg/kg and assigned the Central Valley a five-year average total mercury load allocation of 330 kg/yr at Mallard Island or a decrease of 110 kg/yr in mercury sources to the Delta (Johnson and Looker, 2004; SFBRWQCB, 2006). Compliance with the allocation can be assessed by one of two methods:

> "First, attainment may be demonstrated by documentation provided by the Central Valley Water Board that shows a net 110 kg/yr decrease in total mercury entering the Delta from within the Central Valley region. Alternatively, attainment of the load allocation may be demonstrated by multiplying the flow-weighted suspended sediment mercury concentration by the sediment load measured at the RMP Mallard Island monitoring station. If sediment load estimates are unavailable, the load shall be assumed to be 1,600 million kg of sediment per year. The mercury load fluxing past Mallard Island will be less than or equal to 330 kg/yr after attainment of the allocation."
> (San Francisco Bay Basin Plan, Chapter 7)

Central Valley Water Board staff will recommend to the Central Valley Water Board that the 110 kg total mercury reduction be met by reductions in total mercury entering the Delta from within the Central Valley. Initial reduction efforts should focus on the Cache Creek, Feather River, American River, Cosumnes River and Putah Creek watersheds because they export the largest volume of highly contaminated sediment (see Chapter 8 in this TMDL report and Chapter 4 in the draft Basin Plan Amendment staff report). Load calculation methods and strategies for reducing total mercury loading to San Francisco Bay are discussed more in Chapters 7 and 8 of this report and in the draft Basin Plan Amendment staff report.

Key Points

- The federal Clean Water Act (CWA) requires States to identify water bodies that do not meet their designated beneficial uses and to develop programs to eliminate impairments. States refer to the control program as a Total Maximum Daily Load (TMDL) program. A TMDL is the total maximum daily load of a pollutant that a water body can assimilate and still attain beneficial uses.
- The State of California Porter-Cologne Water Quality Control Act requires the Central Valley Water Board to develop a water quality control plan for each water body in the Central Valley that does not meet its designated beneficial uses. The Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (the Basin Plan) is the legal document that describes the beneficial uses of all water bodies in these basins, adopted water quality objectives to protect them, and, if the objectives are not being met, an implementation program to correct the impairment.
- This draft TMDL report addresses scientific peer review comments on the June 2006 draft TMDL report, Central Valley Water Board member comments and questions voiced during the March 2007 workshop, additional input from agencies and stakeholders during the 2008-2009 Stakeholder Process, and supplementary evaluations to support the Basin Planning effort described in the draft Basin Plan Amendment staff report. After staff has addressed any public comments on this draft TMDL and Basin Plan Amendment staff reports, the final draft Basin Plan Amendment staff report will be presented to the Central Valley Water Board for their consideration later in 2010.
- In 1990 the Central Valley Water Board identified the Delta as impaired by mercury because fish had elevated levels of mercury that posed a risk for human and wildlife consumers. In addition, the San Francisco Bay mercury control program identified Central Valley outflows via the Delta as one of the principal sources of total mercury to San Francisco Bay and assigned the Central Valley a load reduction of 110 kg/yr. Therefore, the final mercury TMDL control plan for the Delta must ensure protection of human and wildlife health in the Delta and meet the San Francisco Bay load allocation for the Central Valley.
- The scope of the Delta methylmercury TMDL includes all waterways within the legal Delta boundary and the Yolo Bypass north of the Delta. This TMDL addresses both methyl and total mercury. Reductions in methylmercury concentrations in ambient water are required to reduce methylmercury concentrations in fish. Reductions in total mercury loads are needed to maintain compliance with the USEPA’s criterion of 50 ng/l; to prevent increases in total mercury discharges from causing increases in water and fish methylmercury in the Delta, thereby worsening the impairment; to meet the San Francisco Bay TMDL allocation to the Central Valley; and to reduce methylmercury production in Delta waterways.
- Elevated fish mercury concentrations occur along the periphery of the Delta while lower body burdens are measured in the central Delta. Concentrations are greater than recommended as safe by the USEPA and USFWS at all locations except in the central Delta. Percent reductions in fish methylmercury levels ranging from 0% to 80% in the peripheral Delta subareas will be needed to meet the numeric targets for wildlife and human health protection.

3 POTENTIALLY CONTROLLABLE METHYLATION PROCESSES IN THE DELTA

The primary problem with mercury in the Delta's aquatic ecosystems can be defined as biotic exposure to methylmercury (Wiener *et al.*, 2003a). Therefore, decreasing biotic exposure to methylmercury is the ultimate goal of the Delta methylmercury TMDL and implementation program. Several published papers provide comprehensive reviews of the current knowledge of the methylmercury cycle (e.g., Wiener *et al.*, 2003a and 2003b; Tetra Tech, Inc., 2005a; LWA, 2002). This chapter focuses on the processes that are potentially controllable in the Delta. The concepts summarized in this chapter guided the development of the methylmercury TMDL for the Delta, particularly the linkage analyses (Chapter 5), methyl and total mercury source analyses (Chapters 6 and 7), and recommended methylmercury allocations and total mercury limits (Chapter 8). Data gaps and uncertainties associated with each factor are identified in this chapter and then addressed further by recommendations for source characterization and control studies in Chapter 4 of the draft Basin Plan Amendment staff report.

Methylmercury concentrations in aquatic ecosystems are the result of two competing processes: methylation and demethylation. Methylation is the addition of a methyl group (CH_3) to an inorganic mercury molecule (Hg^{+2}). Sulfate reducing bacteria are the primary agents responsible for the methylation of mercury in aquatic ecosystems (Compeau and Bartha, 1985; Gilmour *et al.* 1992). Small amounts of methylmercury also may be produced abiotically in sediment (Falter and Wilken, 1998). Maximum methylmercury production occurs at the oxic-anoxic boundary in sediment, usually several centimeters below the surface. Although less common, methylmercury also may be formed in anaerobic water (Regnell *et al.*, 1996 and 2001). In this case, mercury-methylating microbes move from the sediment to the overlying water and the resulting methylmercury becomes available to the biotic community when aerobic and anaerobic waters mix. Methylmercury is a byproduct of the metabolism of sulfate-reducing bacteria. The amount of methylmercury produced is a function of the amount of active bacteria, their available food, and conditions that affect bacterial growth, such as temperature and pH. Given conditions and food positive for growth, sulfate-reducing bacteria will produce methylmercury even if methylmercury is present in the surrounding environment (i.e., methylmercury production is not controlled by chemical equilibrium).

Demethylation is both a biotic and abiotic process. Both sulfate reducing and methanogen-type bacteria have been reported to demethylate mercury in sediment with maximum demethylation co-occurring in the same zone where maximum methylmercury production is located (Marvin-DiPasquale *et al.*, 2000). Photodegradation of methylmercury in the water column also has been observed (Sellers *et al.*, 1996; Byington *et al.*, 2005; Gill, 2008a). While not well studied, the rates of both biotic and abiotic demethylation appear important in controlling net methylmercury concentrations in aquatic ecosystems (Sellers and Kelly, 2001; Marvin-DiPasquale *et al.*, 2000).

Factors controlling sediment methylmercury production have been the subject of intense scientific research (for reviews see Wiener *et al.*, 2003b and Benoit *et al.*, 2003). Sediment factors and landscape events important in net methylmercury production include:

- Sulfate and pH concentration of the overlying water (Gilmour *et al.*, 1998; Miskimmin *et al.*, 1992; Krabbenhoft *et al.*, 1999);

- Percent organic content of the sediment (Krabbenhoft *et al.*, 1999; Miskimmin *et al.*, 1992; Hurley *et al.*, 1998; Heim *et al.*, 2003; Slotton *et al.*, 2003);
- Creation of new water impoundments (Verdon *et al.*, 1991; Bodaly *et al.*, 1997);
- Amount and kind of inorganic mercury present in the sediment (Krabbenhoft *et al.*, 1999; Bloom, 2003); and
- Amount of permanent or seasonally flooded wetland in a watershed (Krabbenhoft *et al*., 1999; Brumbaugh *et al*., 2001; St Louis *et al*., 1994 and 1996; Hurley *et al*., 1995).

Sediment factors and landscape events important in net methylmercury loss in the Delta include:

- Deposition of particle-bound methylmercury in the water column; and
- Photodegradation of methylmercury in the water column.

The significance of deposition and photodegradation in the Delta were reported in the second set of CALFED mercury reports released in 2008 (Stephenson *et al.*, 2008; See Section 3.6)

The level of oxygenation in a water body also affects methylmercury production. The San Francisco Bay Regional Water Quality Control Board required the Santa Clara Water District to test methylmercury controls in three of its reservoirs and to report monitoring results (SFBRWQCB, 2008). Levels of methylmercury in the water column of Lake Almaden decreased significantly after the Santa Clara Valley Water District installed solar-powered water circulators (SCVWD IMC, 2009). Aeration has not been specifically tested in the Delta as a measure to reduce methylmercury concentrations, but may be effective in some situations, such as dredged material settling ponds.

The following sections focus on potentially controllable processes for within-channel methylmercury sources (e.g., wetlands and open-water habitat). Additional point and nonpoint sources are described in Chapters 6, 7 and 8. The organic content of the sediment and the pH of the overlying water are not discussed further as neither appears controllable in the Delta.

3.1 Sulfate

Sulfate is used by sulfate reducing bacteria as the terminal electron acceptor in the oxidation of organic material. Sulfate additions have been observed to both stimulate (Gilmour *et al.*, 1992; King *et al.*, 2002) and inhibit (Benoit *et al.*, 1999; Gilmour *et al.*, 1998) methylmercury production. Addition of sulfate is predicted to stimulate methylmercury production when it is limiting. In contrast, sulfate amendments may inhibit production when excess sulfide is present. Sulfide is the primary byproduct in the reduction of sulfate and increasing sulfide concentrations may cause inhibition by either decreasing the amount of neutrally charged dissolved mercury-sulfide complexes[9] (Benoit *et al.*, 1999 and 2001, but see Kelley *et al.*, 2003, for conflicting results) or by precipitating insoluble mercuric sulfide (Compeau and Bartha, 1985).

[9] Dissolved, neutrally charged mercury is the only form that readily crosses microbial cell membranes.

Two factors influencing sulfate concentrations in the Delta are the water quality objectives for electrical conductivity (EC) and the ratio of San Joaquin River to Sacramento River water. Both are controllable water quality factors and result from water management decisions made by the State of California. Table 3 of Water Rights Decision 95-1WR stipulates maximum ambient electrical conductivity values for various locations in the Delta by month and water year type (SWRCB, 1995). Electrical conductivity in the Delta is primarily a function of freshwater outflow and seawater intrusion.[10] Water Right Decision 95-1WR regulates electrical conductivity by specifying both the amount of freshwater outflow and the amount of water exported to southern California. For example, during 2000-2001, the 2 o/oo salinity level[11] in ambient bottom water was located as far seaward as the City of Martinez in March 2000, but migrated as far upstream as Rio Vista in the summer of 2001 (Foe, 2003). The upstream movement of the salinity field had the effect of increasing sulfate concentrations in western Delta water by about ten-fold.

Sulfate concentrations are about seven times higher in the San Joaquin River than in the Sacramento River. At present, the San Joaquin River is almost entirely diverted out of the Delta by way of Old River and Grantline Canal for export to southern California via the state and federal pumping facilities near Tracy. This reduces the proportion of San Joaquin River water in much of the southern and central Delta and allows intrusion of Sacramento River water with lower sulfate concentrations. The Record of Decision for the CALFED Bay-Delta Program committed the State to evaluate and, if practical, begin construction of a series of permanent, operable barriers in the southern Delta to better control the routing of San Joaquin River water (CALFED Bay-Delta Program, 2004b). An indirect consequence of the permanent barriers is that their operation will determine sulfate concentrations in much of the central and southern Delta.

Sulfate amendment studies need to be undertaken with sediment collected throughout the year from the southern, central and western Delta to determine whether the sulfate concentration in the overlying water affect methylmercury production in sediment. Results of these experiments can be considered when evaluating how to manage the permanent, operable barriers in the southern Delta and when considering water right decisions to modify the location of the salinity field in the Delta.

3.2 New Water Impoundments

The creation of new water impoundments has been found to stimulate sediment microbial activity and to increase methylmercury concentrations in sediment, water and biota (Verdon *et al.*, 1991; Bodaly *et al.*, 1997). The State of California has a growing population and a limited water supply for municipal and agricultural use. One alternative under evaluation is the construction of additional reservoir storage. The Record of Decision for the CALFED Bay-Delta Program directs agencies and local interests to continue to evaluate five surface water storage options to improve water management (CALFED Bay-Delta Program, 2004a). These include north of Delta off-stream storage, in-Delta storage, Shasta Lake expansion, Los Vaqueros

[10] Sulfate concentrations in the Sacramento and San Joaquin Rivers varied between 6-14 and 42-108 mg/l in 2000 and 2001 (Foe, 2003) while full strength seawater is 2,700 mg/l (Parsons and Takahashi, 1973).

[11] Salinity is generally reported in terms of parts per thousand (abbreviated o/oo), the number of pounds of salt per 1,000 pounds of water.

Reservoir expansion and upper San Joaquin storage. Environmental planning for each project is underway and should evaluate the potential of each new facility to increase downstream methylmercury concentrations in the Delta.

3.3 Sediment Mercury Concentrations

Methylmercury production has been found to be a function of the total mercury content of the sediment. Methylmercury concentrations[12] adjusted for the organic content of the sediment increased logarithmically with increasing total mercury concentration in a study of 106 sites from 21 basins across the United States (Krabbenhoft *et al.*, 1999). The slope of the relationship was linear to approximately 1 mg/kg total mercury before commencing to asymptote. Similar linear relationships have been observed in the Delta between methyl and total mercury concentrations in sediment (Table 3.1). The statistical significance of the correlation increases when data from one land use type (e.g., marshes) are used. This implies that methylation rates may also be a function of habitat type. The results are consistent with laboratory experiments where increasing concentrations of inorganic mercury were amended into sediment and the evolution of methylmercury monitored. The efficiency of the conversion of total to methylmercury was linear to about 1 mg/kg before commencing to level off (Bloom, 2003; Rudd *et al.*, 1983).

Mercury concentrations in fish at contaminated sites decline after control measures are instituted to reduce incoming mercury loads (Table 3.2). Most sites studied to date are industrial facilities that discharge to fresh water and have operated for relatively short periods.[13] The initial decrease in fish tissue concentration near the source of contamination is often fast with about a 50% decline in the first five to ten years. However, after a rapid initial decrease, concentrations tend to stabilize with little, if any, subsequent decline (Turner and Southworth, 1999; Takizawa, 2000; Lodenius, 1991; Lindestrom, 2001; Francesconi *et al*., 1997). The new equilibrium value is usually higher than in adjoining uncontaminated waterways and is also often greater than what is recommended as safe for human consumption (Turner and Southworth, 1999; Parks and Hamilton, 1987; Lodenius, 1991; Lindestrom, 2001; Francesconi *et al*., 1997; Becker and Bigham, 1995). The reasons are unclear but may be because small amounts of mercury are still entering from terrestrial sources (Turner and Southworth, 1999) or because of difficulties in bringing sediment concentrations down to background levels (Francesconi *et al*., 1997; Jernelov and Asell, 1975). If contamination has spread to areas more distant than the immediate facility, then reductions in fish tissue concentrations are much slower (Southworth *et al*., 2000). Absent from the literature are reports on remediation of pollution from mercury mining. The magnitude and duration of mercury and gold mining in California, coupled with the extensive distribution of contamination, will likely make recovery much slower than at industrial sites (Table 3.2).

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[12] Radiotracer experiments in Florida Everglade sediment demonstrate that methylmercury production is positively correlated with bulk sediment methylmercury concentrations (Gilmour *et al.*, 1998). Moreover, the spatial pattern of methylmercury production was strongly correlated with aqueous and biotic concentrations, suggesting that surficial sediment concentrations could be used as an analog for *in situ* methylmercury production and flux into the overlying water. Bulk methylmercury sediment concentrations are now widely used as an index of methylmercury production (Krabbenhoft *et al.*, 1999; Bloom *et al.*, 1999 and 2003; Heim *et al.*, 2003; Slotton *et al.*, 2003; Conaway *et al.*, 2003; Benoit *et al.*, 1999).

[13] One to two decades.

As part of the mercury control program for San Francisco Bay, San Francisco Water Board staff established a goal for Bay sediment of 0.2 mg/kg mercury and assigned Central Valley outflows a total mercury load reduction of 110 kg per year to achieve it (Johnson and Looker, 2004; SFBRWQCB, 2006). Waterborne mercury and total suspended sediment loads in the Delta's tributaries are summarized in Chapter 7. Initial management actions of the Delta methylmercury TMDL could consider controlling mercury from watersheds with high methylmercury concentrations in fish, high mercury to suspended sediment ratios and large areas of downstream marsh. The initial goal would be to meet the San Francisco Water Board's goal of 110 kg total mercury reduction per year, but additional load reductions eventually may be needed to achieve compliance with the recommended fish tissue methylmercury targets for the Delta (Chapter 4).

Table 3.1: Field Studies Demonstrating a Positive Correlation Between Total Mercury and Methylmercury in Freshwater Surficial Sediment

Location [(a)]	R^2	P-Value	Comments	Author
Sacramento-San Joaquin Delta Estuary	0.2	<0.01	All habitats in Delta combined.	Heim *et al.*, 2003
Sacramento-San Joaquin Delta Estuary	0.52	<0.001	Only marsh habitats.	Heim *et al.*, 2003
Sacramento-San Joaquin Delta Estuary	0.37	<0.001	Comparisons inside and outside of flooded Delta Islands.	Slotton *et al.*, 2003
Elbe River	0.69	<0.0001	Germany.	Hintelmann & Wilken, 1995
Patuxent River Estuary	0.61	<0.05	Sub embayment of Chesapeake Bay.	Benoit *et al.*, 1998
National Survey	0.62	<0.0001	Log/log relationship normalized to percent organic carbon at 106 sites in 21 basins across the United States.	Krabbenhoft *et al.*, 1999
Lake Levrasjon	0.64	<0.05	Southern Sweden.	Regnell & Ewald, 1997

(a) The majority of the sediment in each study had a mercury content less than 1 ppm.

Table 3.2: Change in Fish Tissue Mercury Concentration After Initiation of Source Control.

Location	Mercury Source	Biotic Change	Control Measures	References
Oak Ridge National Laboratory, Tennessee	Weapons Facility	Sunfish at discharge point declined from 2 to 1 mg/kg in 5 yrs; half mile downstream sunfish declined from 0.9 to 0.7 mg/kg in 9 yrs; no change in tissue 2 and 5 miles downstream.	Reduced discharge, excavated portion of flood plain.	Turner & Southworth, 1999; Southworth *et al*., 2000
Lake St. Clair, Michigan	Two Chloralkali Plants	Walleye fish declined from 2.3 to 0.5 mg/kg in 25 yrs	Reduced/eliminated discharge	Turner & Southworth, 1999.
Abbotts Creek, North Carolina	Battery Manufacturing plant	Fish declined from 1 to 0.5 mg/kg in 11 yrs	Treated groundwater, reduced/eliminated discharge, removed contaminated soil, natural sediment burial	Turner & Southworth, 1999
Saltville, Virginia	Chloralkali Plant	Rockfish declined from 3.5 to 1 mg/kg in 20 yrs	River sediment dredged, rock bottom grouted, rip-rap river bank, pond seepage treated with activated carbon	Turner & Southworth, 1999
Howe Sound, British Columbia, Canada	Chloralkali Plant	Dungeness crab declined from 2 to 0.2 mg/kg in 5 yrs. No subsequent change	Reduced/eliminated discharge, treated groundwater	Turner & Southworth. 1999
Little Rock Lake, Wisconsin	Atmospheric deposition	Yellow Perch declined 30% in 6 yrs	Reduced atmospheric mercury input by 60%.	Hrabik & Watras, 2002.
Minimata, Japan	Chloralkali Plant	Fish declined from 9.0 to 0.4 mg/kg in 8 yrs; no further change.	Eliminated discharge; dredged and disposed of sediment.	Takizawa, 2000
Clay Lake, Ontario, Canada	A chloralkali plant and a wood pulp mill.	Walleye fish declined from 15.1 to 2.0 mg/kg in 20 yrs. Background concentration is 0.6 mg/kg.	Eliminated discharge; natural burial of contaminated sediment	Parks & Hamilton, 1987; Turner & Southworth, 1999.
Ball Lake, Ontario, Canada (downstream of Clay Lake)	Same as above	Walleye fish declined from 2.0 to 1.4 mg/kg in first 5 yrs. Northern Pike from 5.1 to 1.8 mg/kg. No change in Lake Whitefish.	Same as above	Armstrong & Scott, 1979
Lake Kirkkojarvi, Finland	Phenylmercury in slimicide in pulp mill	4 and 1-kg Northern Pike declined from 3.6 to 2.1 and from 1.5 to 0.8 mg/kg in 20 yrs. All reductions happened in first 10 yrs. Background concentration in 1-kg pike is 0.4 mg/kg.	Reduced discharge, natural burial	Lodenius, 1991
Lake Vanern, Sweden	Chloralkali Plant	5-yr old Northern Pike declined from 1.4 to 0.6 mg/kg in 25 yrs. Most of decrease occurred in first 10-15 yrs. Background concentrations in Pike are 0.4 mg/kg	Reduced/eliminated discharge, natural burial	Lindestrom, 2001
Princess Royal Harbor, Australia (Marine water)	Superphosphate Processing Plant	Mercury in 8 marine fish species declined by about 50% in 9-yrs. Most of decrease happened in first 4-yrs. Tissue concentrations are still about twice background.	Eliminated discharge, natural burial	Francesconi *et al*., 1997
Onondaga Lake, New York	Municipal and industrial discharge	Mercury in six fish species declined by 60 to 80 % in 22 yrs. Tissue concentrations are still about twice background.	Eliminated discharge, natural burial	Becker & Bigham, 1995.
North Carolina, Quebec, Finland, Manitoba, Labrador and Newfoundland	Reservoir creation	Fish tissue levels declined to normal after 3 to 30 years.	None	As reviewed in French *et al*., 1998.

3.4 Forms of Mercury

There are primarily two different forms of mercury transported into the Delta with potentially different methylation rates. The first form is mercury mine waste from the Coast Range. Most of this material is thought to be mercuric sulfide, cinnabar and metacinnabar (Bloom, 2003). Mercury mine waste enters the Delta from mine-impacted coast range creeks such as Putah and Cache Creeks. The second form is elemental mercury lost from placer and hardrock gold mining operations in the Sierra Nevada Mountains. Elemental mercury enters the Delta in Sacramento, Mokelumne and San Joaquin River water that drains from the northern and southern gold fields. [Additional sources of mercury are described in Chapter 7.]

Mercury from gold mining appears to be more biologically available than material from mercury mines. The evidence is twofold. First, Frontier Geosciences conducted a 1-year microcosm incubation study with both gold and mercury mine waste to determine the relative methylation efficiency of each (Bloom, 2003). Mercury from gold mining was found to have the higher methylation rate. Second, the ratio of methyl to total mercury in natural sediment is assumed to be a field measure of methylation efficiency (Gilmour *et al.*, 1998; Krabbenhoft *et al.*, 1999; Bloom *et al.*, 1999 and 2003). Heim and others (2003) collected sediment at multiple locations in Cache Creek (representative of mercury mine waste) and the Cosumnes River (representative of gold mine material) on three occasions (October 1999, May 2001 and October 2001) to determine methyl and total mercury concentrations and methylation efficiencies. The highest methyl to total mercury ratios were consistently observed in Cosumnes River material. These results are consistent with the conclusions of Bloom (2003) and suggest that floured elemental mercury from gold mining in the Sierra Nevada is more readily methylated than is cinnabar from the Coast Range.

Heim and others (2003) also collected sediment samples at multiple locations in Cache Creek. The ratio of methylmercury to total mercury increased with increasing distance from the mercury mining districts. The authors speculate that diagenic weathering-type processes are changing the form of the mercury and increasing its methylation efficiency as the material is slowly transported away from the mines. The precise mechanisms are not known but may include the formation of soluble polysulfide complexes (Paquette and Heltz, 1995) and dissolution of cinnabar by humic and fulvic acids (Wallschläger *et al.*, 1998; Ravichandran *et al.* 1998). Both processes should increase the efficiency of the conversion of inorganic to organic mercury. No similar weathering type experiments have been conducted on Sierra Nevada gold mine-derived mercury. The Cache Creek findings suggest that there is currently insufficient understanding of mercury weathering processes to justify developing control programs that preferentially target controlling gold-mine waste material.

3.5 Wetlands

Research in the Delta and elsewhere has found that wetlands are sites of efficient methylmercury production (Slotton *et al.*, 2003; Heim *et al.*, 2003; St. Louis *et al.*, 1994, 1996; Gilmour *et al.*, 1998). In fact, one of the best predictors of methylmercury concentrations in water and in biota is the amount of wetland present in upstream watersheds (Krabbenhoft *et al.*, 1999; Wiener *et al.*, 2003b). The Record of Decision for the CALFED Bay-Delta Program commits it to restore 30,000 to 45,000 acres of fresh, emergent tidal wetlands, 17,000 acres of fresh, emergent nontidal wetlands, and 28,000 acres of seasonal wetlands in the Delta by 2030 (CALFED Bay-Delta Program, 2000b). This is a total of 75,000 to 90,000 acres of additional seasonal and permanent wetlands in the Delta, which represents about a three to four times increase in wetland acreage from current conditions. Many of the proposed restoration sites are downstream of mercury-enriched watersheds. Marsh restoration efforts below mercury enriched watersheds are proposed for the following locations: Yolo Bypass downstream of Cache and Putah Creeks; Dutch Flats downstream of the Mount Diablo Mercury mine in the Marsh Creek watershed; and Staten Island and the Cosumnes River Wildlife Refuge near the confluence of the Cosumnes River and Mokelumne River. Extensive restoration efforts in the Delta have the potential to increase methylmercury exposure for people and wildlife. This potentially significant adverse environmental impact was identified in CALFED's programmatic ROD's CEQA evaluation.

Even though much of the research has found that wetlands act as sources of methylmercury, recent data indicate that some wetlands may act as net methylmercury sinks. Table 3.3 provides a summary of methylmercury production characteristics from different types of wetlands in the Delta region. In addition, a technical review of the June 2006 TMDL Report described a study conducted in southern Florida, in which different wetland and open water sites were found to contain varying levels of methylmercury (Tetra Tech, Inc., 2006). More research is needed to understand the processes that affect a wetland's methylmercury production, so that wetland restoration can occur with minimal methylmercury production increases.

Table 3.3: Summary of Wetland Methylmercury Production Characteristics.

Watershed	Site [(a)]	Wetland Type	MeHg Characteristics [(b)]
Delta	Twitchell Island (1)	2 Permanent (test ponds)	Both sources
	Browns Island (2)	Permanent, tidal	Small source
	Sycamore Slough (3)	Permanent, tidal	Sink
	Grizzly Island (Suisun Marsh) (4)	2 Seasonal	Source
Cache Creek	Anderson Marsh (5)	Permanent	Source
	Cache Creek Nature Preserve (6)	Permanent	Source
Mud Slough	San Luis Wildlife Refuge (7)	2 Permanent	Both neutral
		6 Seasonal	All sources
Suisun Marsh	First Mallard Branch (interior marsh) (3)	Permanent, tidal	Source
	Suisun Slough (mouth) (3)	Permanent, tidal	Sink

(a) Study citations: (1) Sassone *et al*., 2006; Sassone *et al*., 2008 (2) Fleck *et al*., 2007; (3) Heim et al., 2007; (4) Stephenson *et al*., 2008; (5) CVRWQCB, unpublished data; (6) Slotton and Ayers, 2001; (7) Stephenson *et al*., 2007.

(b) Wetlands that act as net producers of methylmercury are noted as "sources"; wetlands that act as sinks for methylmercury (e.g., more methylmercury is imported than exported) are noted as "sink"; and wetlands that apparently acted as neither a source nor sink for methylmercury are noted as "neutral".

3.6 Methylmercury Loss by Sedimentation and Photodemethylation

As water moves across the Delta from the Sacramento River to the pumps, settling of methylmercury bound to particles reduces aqueous methylmercury concentrations (Stephenson and Bonnema, 2008). Losses of methylmercury and particles were shown in samples collected as water from both the Sacramento and San Joaquin Rivers moved through the Delta (Heim *et al.*, 2008). The transect sampling by Heim and colleagues tracked the two largest sources of water entering the Delta and identified losses at two points: downstream of the convergence of the Sacramento River with Cache and Steamboat Sloughs and entry of San Joaquin River water into the San Joaquin Deep Water Ship Channel. The methylmercury loss in the San Joaquin River was not observed in some winter and spring sampling events. Data collected during the recent CalFed mercury project (Heim *et al.,* 2008; Foe *et al.*, 2008) were used in a particle transport model that demonstrated methylmercury movement in multiple flow paths across the Delta (Stephenson *et al*., 2008b). Methylmercury loss rates due to photodemethylation and particle settling varied by flow path and season.

Methylmercury loads from in-channel sources such as wetlands, ponds, and settling basins, as well as retention basins in urban areas, may be able to be controlled by enhancing their sediment trapping efficiency. During stakeholder meetings in 2009, entities responsible for methylmercury from managed wetlands and irrigated agriculture began gathering information and considering possible ways to enhance sedimentation of methylmercury. Ideas that could be investigated during studies in the first phase of the Delta mercury control program include: adding a sill or specific vegetation to trap sediment, creating small settling basins within drainage canals, and managing flow and depth within a pond or wetland system to maximize settling (Stephenson, 2009).

The results of the particle transport modeling (Stephenson *et al*., 2008b) could lead to changes in how the Delta subareas are delineated (see Section 2.2.2 in Chapter 2). For example, during a model run for August 2005 (Stephenson, 2009, video provided through pers. comm.), the particle tracking model indicates the San Joaquin River subarea could be re-delineated to include more of the Central Delta subarea, and the Sacramento River subarea could be re-delineated to include a portion of the southern Yolo Bypass subarea. If funding can be acquired, staff hopes to work with the particle transport model study authors to evaluate a variety of typical hydrographic periods and, if needed, re-delineate the Delta subareas to better reflect the water and sediment sources that drive water and fish methylmercury concentrations in different Delta areas.

Key Points

- The problem with mercury in the Delta's aquatic ecosystems can be defined as biotic exposure to methylmercury. Therefore, decreasing biotic exposure to methylmercury is the ultimate goal of the Delta methylmercury TMDL and implementation program.
- The implementation plan should focus on sources and processes that are potentially controllable in the Delta. Potentially controllable sediment factors and landscape events important in net methylmercury production include: water rights salt standards in the Delta; creation of new water impoundments; amount of inorganic mercury present in the sediment; and management of permanent or seasonally flooded wetland in a watershed.

4 NUMERIC TARGETS

Water quality targets for mercury in fish were calculated to protect beneficial uses of the water and aquatic resources of the Delta. The targets are intended to reduce the risks to humans and wildlife that consume fish and other aquatic organisms from the Delta that contain methylmercury. This chapter first describes the derivation of species-specific targets based on a suite of fish types to protect humans and wildlife. The Central Valley Water Board staff proposes three targets for the protection of human and wildlife health: 0.24 mg/kg (wet weight) in muscle tissue of large trophic level four (TL4) fish such as bass and catfish; 0.08 mg/kg (wet weight) in muscle tissue of large TL3 fish such as carp and salmon; and 0.03 mg/kg (wet weight) in whole trophic level 2 and 3 fish less than 50 mm in length. In addition, staff proposes an implementation goal of 0.24 mg/kg methylmercury, wet weight, in standard 350-mm largemouth bass. As described in Chapter 5, this implementation goal can be linked to aqueous methylmercury to develop an implementation goal for methylmercury in unfiltered ambient water, which in turn can be used to determine methylmercury source reductions needed to achieve the proposed targets for methylmercury in fish.

In addition to addressing sources of methylmercury to the Delta, the Delta mercury control program addresses total mercury sources to the Delta and San Francisco Bay. The San Francisco Bay TMDL assigns a load reduction of 110 kg per year from the Central Valley (Johnson and Looker, 2004; SFBRWQCB, 2006). As described in later chapters of this report, the mercury control program for the Delta is designed to achieve the total mercury load reduction required by the San Francisco Water Board, as well as to maintain compliance with the USEPA's CTR for total mercury in freshwater sources and to limit total mercury sources to the Delta to ensure that methylmercury levels in fish do not increase in the future.

4.1 Definition of a Numeric Target

Numeric targets are the specific goals for the TMDL that will enable the protection of the beneficial uses of the Delta and San Francisco Bay. The development of numeric targets involves the following elements:

- Identification of the target media and the basis for using the selected target media to interpret or apply applicable water quality standards.
- Identification of target levels for the selected target media and the technical basis for the target levels.
- Comparison of historical or existing conditions and desired future conditions for the target media selected for the TMDL.

4.2 Clean Water Act 303(d) Listing and Beneficial Use Impairment

The Office of Environmental Health Hazard Assessment issued health advisories recommending that consumers limit their consumption of striped bass and sturgeon from the Delta and Bay because of high methylmercury tissue concentrations (Section 2.4.1). The fish advisory resulted in the Central Valley and San Francisco Water Boards listing the Bay-Delta Estuary as impaired.

By definition, an impaired water body does not support all of its designated beneficial uses. Existing and potential beneficial uses are listed in Table 2.3 in Chapter 2. The Delta provides habitat for warm and cold water species of fish and the aquatic communities associated with them. In addition, the Delta and associated riparian areas provide valuable wildlife habitat. Beneficial uses that are impaired due to high mercury levels include commercial and sport fishing and wildlife habitat.

4.3 Selection of the Type of Target for the Delta

4.3.1 Fish Tissue

Measurements of mercury in the target media should be able to assess fairly directly whether beneficial uses are being met. Several media for numeric targets were considered, including sediment, water column and biota. The major beneficial use of the Delta that is currently unmet is its use as a safe fishery for humans and wildlife. A target of mercury in fish tissue was determined to be the most appropriate because it provides the most direct assessment of fishery conditions and improvement. Fish tissue data have been collected between 1969 and 2002 in the Delta. Existing data for fish species consumed by humans and wildlife provide a baseline against which future improvements can be measured.

Targets are developed for **methylmercury** in fish tissue because it is the most toxic form of mercury. It is also the form to which humans and wildlife may be exposed in the Delta at levels sufficient to cause adverse effects. The cost for methylmercury analysis is greater than that for total mercury; therefore, most data available are for total mercury in fish tissue. Independent research demonstrates that most mercury (85-100%) in fish muscle is methylmercury (Becker and Bigham, 1995; Slotton *et al.*, 2004). For the purposes of the TMDL, Central Valley Water Board staff assumes that all the mercury measured in Delta fish is methylmercury.

4.3.2 San Francisco Bay Numeric Target

The Delta TMDL is structured to meet the San Francisco Bay mercury TMDL's total mercury allocation for Central Valley outflows to the Bay. San Francisco Water Board staff developed a target for San Francisco Bay sediment mercury concentration of 0.2 mg/kg and assigned the Central Valley a five-year average total mercury load allocation of 330 kg/yr at Mallard Island or a decrease of 110 kg/yr in mercury sources to the Delta. The 2004 San Francisco Bay mercury TMDL staff report provides a detailed derivation of the San Francisco Bay sediment target and allocation for the Central Valley (Johnson and Looker, 2004; SFBRWQCB, 2006). Strategies for reducing the total mercury loading to San Francisco Bay are discussed in Chapter 8 in this TMDL report and Chapter 4 in the draft Basin Plan Amendment staff report.

4.3.3 Water Criteria

The California Toxics Rule (CTR) mercury criterion applies to the Delta (see Section 2.3.2.2). This criterion of 50 ng/l total recoverable mercury in water is intended to protect the health of humans consuming contaminated organisms and drinking water. The CTR value may not be sufficiently protective of humans consuming fish from the Delta because of the low bioconcentration factors used to derive the CTR value. Central Valley Water Board staff considers fish tissue targets to be more stringent than the CTR criterion.[14] Although the CTR criterion may be less protective than the fish tissue targets discussed below, the TMDL was designed to comply with the CTR mercury criterion. Compliance with the CTR criterion through the TMDL is discussed in the total mercury source assessment (Chapter 7) and total mercury limits (Chapter 8) sections of this report.

4.4 Fish Tissue Target Equation and Development

Key variables that are incorporated into the calculation of fish tissue targets are:

- Acceptable daily dose level of methylmercury;
- Body weight (bwt) of the consumer;
- Trophic level or size of fish consumed; and
- Rate of fish consumption.

These components can be related using a basic equation (OEHHA, 2000; USEPA, 1995c) as follows.

Equation 4.1:

$$\frac{\text{Safe daily intake * Consumer's body weight}}{\text{Consumption rate}} = \text{Acceptable level of mercury in fish tissue}$$

At or below the safe daily intake of methylmercury, consumers are expected to be protected from adverse effects. An acceptable intake level is also called a reference dose (RfD). An RfD is expressed as an average daily rate (micrograms of mercury per kilogram body weight per day) of mercury intake. In general, an RfD is calculated by using studies of exposure in specific populations to determine a threshold level of exposure below which adverse effects did not occur. The threshold level is then divided by uncertainty factors that lower the value to the final reference dose. Uncertainty factors account for differences in metabolism and sensitivity between individuals, lack of toxicity information in available studies, or other unknowns.

In the calculation of its recommended methylmercury criterion to protect human health, USEPA added a relative source contribution (RSC) component to the equation to account for methylmercury from other sources (USEPA, 2001). Humans are exposed to methylmercury

[14] The weighted average practical bioconcentration factor (PBCF) used to develop the CTR mercury criterion is 7342.6 (USEPA, 2000b). For the Delta, bioaccumulation factors (BAF) for large trophic 4 fish are in the range of 50,000 to 300,000. These BAFs are the ratios of mercury in fish to the concentration of total recoverable mercury in water. The Delta bioaccumulation factors indicate that piscivorous fish species in the Delta accumulate higher concentrations of mercury than USEPA's PBCF.

from commercial fish as well as locally caught fish. Human intakes of methylmercury from all other sources (air, drinking water, soil, and foods other than fish and seafood) are considered negligible. The RSC represents that portion of methylmercury exposure that will not be controlled by cleanup actions directed to a particular water body. Because piscivorous wildlife species are assumed to obtain all of their fish or other aquatic prey from the local water body, no RSC adjustment is used for the wildlife calculations. As with humans, the direct intake of methylmercury by piscivorous wildlife from air or water is negligible relative to intake from fish and aquatic organisms (USEPA, 1997a).

The consumption rate can be separated into rates of consumption of fish from each trophic level. Adjusting for multiple consumption rates and the RSC, the basic equation appears as follows.

Equation 4.2:

$$\frac{(\text{Safe intake} - \text{RSC}) * \text{body weight}}{(\text{CRate}_{TL2} + \text{CRate}_{TL3} + \text{CRate}_{TL4})} = \text{Acceptable level of mercury in Delta fish tissue}$$

Where: CRate_{TL2} = consumption rate of fish from Trophic Level 2

CRate_{TL3} = consumption rate of fish from Trophic Level 3

CRate_{TL4} = consumption rate of fish from Trophic Level 4

Safe levels of methylmercury in fish tissue that protect wildlife are presented first in this report, followed by the human health targets. The order of presentation and in-depth discussion of wildlife methodology are not intended to suggest greater importance of wildlife targets relative to human health targets. Rather, wildlife targets are discussed first because the safe fish tissue levels are based on average consumption rates that are assumed to be constant. Human consumption rates, however, vary widely by individual. For targets to protect human consumers, consumption rate options are incorporated into the calculations.

4.5 Wildlife Health Targets

Birds and mammals most likely at risk for mercury toxicity are primarily or exclusively piscivorous. Those identified for the Delta are: American mink, river otter, bald eagle, kingfisher, osprey, western grebe, common merganser, peregrine falcon, double crested cormorant, California least tern, and western snowy plover[15] (USEPA, 1997a; CDFG, 2002). Bald eagles, California least terns and peregrine falcons are listed by the State of California or by the USFWS as either threatened or endangered species. The Delta is a foraging and possible wintering habitat for bald eagles (USFWS, 2004). California least terns also forage in the Delta. There is at least one nesting colony of these terns within the Delta (USFWS, 2004).

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15 The CDFG *California Wildlife Habitat Relationships* database also reports observations of brown pelicans and clapper rails in the Delta. Both of these species are federally listed as endangered and depend on the aquatic food web. However, it has been confirmed that brown pelicans and clapper rails prefer saltwater habitats and are only occasional visitors to the Delta regions as discussed in this TMDL (Schwarzbach, 2003; CDFG, 2005). Peregrine falcon are included because they consume piscivorous waterfowl.

Although most of the Delta habitat is unlike that preferred by peregrine falcons for nesting, several peregrine falcon pairs have nested on bridges in the area (Linthicum, 2003).

Acceptable fish tissue mercury levels for wildlife species can be calculated using daily intake levels, body weights and consumption rates. Parameters needed to estimate daily methylmercury exposures and safe levels of methylmercury in prey for wildlife are given in Table 4.1. Mercury studies conducted in the laboratory and field are used to derive RfD for birds and mammalian wildlife. The following section uses these RfDs to calculate fish tissue targets to protect the health of wildlife in the Delta.

4.5.1 Reference Doses, Body Weights & Consumption Rates

The reference dose for mammalian wildlife species of 0.018 mg methylmercury/kg bwt/day is based on studies in which mink were fed methylmercury at varying doses and evaluated for neurological damage, growth and survival (USEPA, 1995a; USEPA, 1997b). Studies of mallard growth and reproduction following methylmercury exposure were used to determine a methylmercury reference dose for birds of 0.021 mg/kg bwt/day (USEPA, 1997b). For each of reference doses, the lowest toxic dose was divided by three (uncertainty factor) to account for differences in species' and individuals' reactions to mercury and produce a dose level at which harmful effects are not expected (USFWS, 2003).

Average body weights of adult females are used because the most sensitive endpoints of methylmercury toxicity are related to reproductive success. The USFWS provided guidance to Central Valley Water Board staff regarding the species of concern and their exposure parameters (USFWS, 2002, 2003 and 2004).

4.5.2 Safe Methylmercury Levels in Total Diet

Fish tissue mercury levels that would result in methylmercury intakes by piscivorous wildlife at or below safe intake levels are calculated in two steps. First, safe levels of methylmercury in the total diet of each wildlife species are calculated (Table 4.2). The total diet safe level represents the concentration of methylmercury, as an average in all prey consumed, needed to keep the organism's daily intake of methylmercury below the reference dose. Total diet safe levels were calculated using the exposure parameters for wildlife species and Equation 4.1. In the second step, the total diet safe level is translated into protective levels of methylmercury in various components of an organism's diet (Table 4.3). An example calculation of the total safe diet level for mink is shown below:

$$\frac{\text{Mammalian reference dose * Mink body weight}}{\text{Mink fish consumption rate}} = \text{Total diet safe level}$$

$$\frac{18\ \mu\text{g MeHg/kg day * 0.60 kg}}{140\ \text{g/day}} = 0.077\ \mu\text{g MeHg/g total diet (0.077 mg/kg)}$$

Table 4.1: Exposure Parameters for Fish-Eating Wildlife

Species [a]	**Body weight** [b]	**Total Food Ingestion Rate** [c]	**Trophic Level 2 Aquatic Prey**	**Trophic Level 3 Aquatic Prey**	**Trophic Level 4 Aquatic Prey**	**Piscivorous Bird Prey**	**Omnivorous Bird Prey**	**Other Foods** [d]	**Size of Prey**
	kg	g/day, wet wt	g/day, as % of diet	g/day, as % of diet	g/day, as % of diet	g/day, as % of diet	g/day, as % of diet	g/day, as % of diet	
Mink	0.60	140	-	140 (100%)	-	-	-	-	most prey 50-150mm; females catch smaller prey than males (USEPA, 1995b)
River otter	6.70	1124	-	899 (80%)	225 (20%)	-	-	-	heterogeneous, 20-500 mm (USEPA, 1995b); majority <150 mm but commonly catch large TL4 fish.
California least tern	0.045	31	-	31 (100%)	-	-	-	-	mostly < 50 cm, nearly all fish
Western snowy plover	0.041	33.3	8.3 (25%)	-	-	-	-	25 (75%)	mainly aquatic and terrestrial invertebrates. Assume TL2 aquatic prey is 25% of diet (USFWS, 2003)
Belted kingfisher	0.15	68	-	68 (100%)	-	-		-	generally less than 105 mm; up to 180 mm (Hamas, 1994)
Common merganser [e]	1.23	302	-	302(100%)	-	-	-	-	most prey <150 mm (USEPA, 1995b; Hatch & Weseloh, 1999)
Double-crested cormorant [f]	1.74	390	-	390 (100%)	-	-	-	-	generally 100-300 mm length; up to 360mm (Mallory & Metz, 1999)
Western grebe [g]	1.19	296	-	296 (100%)	-	-	-	-	USFWS assumed similar to merganser (USFWS, 2004)
Bald eagle [h]	5.25	566	-	328 (58%)	74 (13%)	28 (5%)	74 (13%)	62 (11%)	fish 75-500+ mm; most will be >150 mm (Jackman *et al.*, 1999; USEPA, 1995b).
Osprey [i]	1.75	350	-	315 (90%)	35 (10%)	-	-	-	fish 100-450 mm; most will be >200 mm.
Peregrine falcon [j]	0.89	134	-	-	-	6.7 (5%)	13.4 (10%)	114 (85%)	Does not eat fish.

<u>Table 4.1 Footnotes</u>:

(a) Italics denote species listed as threatened or endangered by state or federal authorities.

(b) Average female body weights are from *Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals Volume II* (USEPA, 1995b), USFWS (2003, 2004), and as noted below.

(c) Total food ingestion rates are from USEPA (1995b) and USFWS (2003; 2004) and as noted below.

(d) Other foods are mainly terrestrial mammal, bird, reptile and invertebrate prey that are presumed to provide negligible amounts of methylmercury.

(e) Merganser body weight and ingestion rate from Schwarzbach and others (2001).

(f) Cormorant body weight is the average for female birds cited in Hatch and Weseloh (1999). This paper also reports daily consumption at 20-25% of body mass. Total ingestion rate of 390 g/day is 22.5% of average female bodyweight.

(g) Female western grebe body weight from Storer and Nuechterlein (1992).

(h) Bald eagle parameters provided by the USFWS (2004). Diet of bald eagles in northern California includes fish, mammals and birds. Using dietary data from Jackman and others (1999), the USFWS estimated the average proportions of prey types. TL3 and TL4 fish comprised 58% and 13% of the total bald eagle diet, respectively. Piscivorous birds, such as gulls, grebes, and mergansers, comprised approximately 5% of the total diet. An additional 13% of the total diet was comprised of other aquatic birds, such as coots, that feed mainly on TL2 organisms. Bald eagles are scavengers and thus consume fish of large sizes (Jackman *et al.*, 1999).

(i) Osprey catch and eat large fish, the majority of which are >200 mm (USEPA, 1995b). In a water body where TL4 sport fish are readily available, osprey diet is assumed to be 10% TL4 fish (USFWS, 2002). Prey size is limited to the maximum size that an osprey can lift out of water.

(j) Peregrine falcons eat a wide variety of birds, including grebes, herons, shorebirds, mergansers, gulls and other birds that accumulate methylmercury from the aquatic food web. USFWS (2004) supports the assumption by Central Valley Water Board staff that approximately 15% of peregrine prey in the Delta area is comprised of piscivorous birds. See the appendices of the Cache Creek TMDL for Mercury staff report for further analysis of peregrine prey and habitat.

Table 4.2: Concentrations of Methylmercury in Total Diet to Protect Delta Wildlife Species

Species	**RfD** (µg/kg bwt-day)	**Body Weight** (kg)	**Total Food Ingestion Rate** (g/day)	**Safe Methylmercury Concentration in Total Diet** (mg/kg in diet)
Mink	18	0.60	140	0.077
River otter	18	6.70	1124	0.11
California least tern	21	0.045	31	0.030
Western snowy plover	21	0.041	33.3	0.026
Belted kingfisher	21	0.15	68	0.046
Common merganser	21	1.23	302	0.086
Double-crested cormorant	21	1.74	390	0.094
Western grebe	21	1.19	296	0.084
Bald eagle	21	5.25	566	0.20
Osprey	21	1.75	350	0.11
Peregrine falcon	21	0.89	134	0.14

Table 4.3: Safe Concentrations of Methylmercury in Fish (mg/kg) by Trophic Level to Protect Wildlife

Species [(a)]	TL 2, < 50 mm	TL 2-3, 50-150 mm	TL 3, 150-350 mm	TL 4, 150-350 mm	TL 3, >150 mm	TL 4, >150 mm
Mink		0.08				
River otter		0.04		0.36		
California least tern	0.03					
Western snowy plover [(b)]	0.10					
Belted kingfisher		0.05				
Double-crested cormorant		0.09				
Common merganser			0.09			
Western grebe			0.08			
Osprey			0.09	0.26		
Bald eagle [(c)]					0.11	0.31
Peregrine falcon [(d)]			(0.17)			

(a) Italics denote species that are listed as threatened or endangered by federal or state authorities.
(b) The snowy plover safe level should be applied to TL2/3 aquatic invertebrates, such as small clams, crabs, polychaetes and amphipods.
(c) To avoid exceeding the bald eagle wildlife value, safe concentrations must be attained in birds as well as fish eaten by bald eagles. The safe levels for average mercury concentrations in omnivorous and piscivorous bird prey are 0.19 and 1.35 mg/kg, respectively. Because bald eagles are scavengers, there is no upper size limit on fish eaten by these birds.
(d) Parentheses denote the TL3 fish level corresponding to the piscivorous bird safe concentration for peregrines. For birds eaten by peregrine falcons, the average concentrations should not exceed 2.2 mg/kg in piscivorous bird prey, respectively.

4.5.3 Calculation of Safe Fish Tissue Levels from Total Diet Values

Wildlife species consume fish and other aquatic prey from various size ranges and trophic levels. In the second step of wildlife target development, safe fish tissue levels are identified for different prey classifications. These classifications are termed “trophic level food groups”. Table 4.3 shows safe fish tissue concentrations needed by the wildlife species and developed for prey within the following trophic level food groups: TL2 fish less than 50 mm in length, 50-150 mm TL2 and 3 fish, 150-350 mm TL3 fish, and TL4 fish greater than 150 mm.

In cases in which an organism’s prey is fairly uniform and from one trophic level, the total diet safe level becomes the average, safe tissue mercury concentration. For organisms that feed from different trophic levels, the proportions of each trophic level in the diet (Table 4.1) are used to determine safe tissue mercury levels for each component of the diet. The species whose prey falls generally into one size category are mink, California least tern, western snowy plover, double crested cormorant, western grebe, kingfisher and common merganser. For these species, the total diet safe level becomes the safe fish tissue level matched to the size and trophic level of prey consumed.

Average, safe fish tissue concentrations for kingfisher, cormorant and mink were determined for the food group size range of 50-150 mm. Although kingfishers typically consume fish less than 105 mm in length, they can eat fish as long as 180 mm (Hamas, 1994; USEPA, 1995b). The range for cormorant prey is 30 to 400 mm, with most fish eaten being less than 150 mm (Hatch and Weseloh, 1999). Most fish caught by mink are in the range of 50-150 mm (USEPA, 1995b).

As the size ranges of prey caught by these three species are similar, one category of TL2/3 fish is appropriate for their protection (USFWS, 2004).

A second food group of TL3 fish in the range of 150-350 mm incorporates safe fish tissue mercury concentrations for prey of common mergansers and western grebes. Most prey caught by mergansers is in the range of 100-300 mm, with catches of fish up to 360 mm observed (Mallory and Metz, 1999). Because body size and foraging strategy of western grebes are similar to those of the merganser, staff assumed the same size range for grebe prey (USFWS, 2004).

Otter, bald eagle and osprey eat fish from multiple trophic level food groups. Methylmercury concentrations vary as a function of size and trophic level of prey. Therefore, different trophic levels of prey will have different acceptable concentrations of methylmercury. For these wildlife species, the total diet safe level (TDSL) can be described as:

Equation 4.3:

$$TDSL = (\%\ diet\ TL_2 * TL2_{conc}) + (\%\ diet\ TL_3 * TL3_{conc}) + (\%\ diet\ TL_4 * TL4_{conc})$$

Where:

% diet TL_2	=	percent of trophic level 2 biota in diet
% diet TL_3	=	percent of trophic level 3 biota in diet
% diet TL_4	=	percent of trophic level 4 biota in diet
$TL2_{conc}$	=	concentration of methylmercury in TL2 biota
$TL3_{conc}$	=	concentration of methylmercury in TL3 biota
$TL4_{conc}$	=	concentration of methylmercury in TL4 biota

In order to solve the above equation for the desired concentrations in TL2, TL3 and TL4 biota, concentrations in two trophic levels are put in terms of the concentration in the lowest trophic level. Equation 4.3 is then rearranged to solve for the lowest trophic level concentration.

In order to express the concentration in a higher trophic level (i.e., TL4) in terms of TL2 concentrations, staff used two types of translators: food chain multipliers (FCM) and trophic level ratios (TLR).[16] FCM and TLR used in the calculation of Delta wildlife targets are shown in Table 4.4. Where possible, site-specific, existing fish concentration data was used to develop the ratios. A similar table of safe fish tissue concentrations to protect wildlife species using a national average bioaccumulation factor (BAF) between TL3 and TL4 of five is presented in Chapter 6 of Mercury Study Report to Congress Vol. 7 (USEPA, 1997b). Details regarding the calculation of the translators and their use were provided by the USFWS (2003 and 2004).

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[16] A food chain multiplier (FCM) is the ratio of methylmercury concentrations in fish of different trophic levels. A FCM represents the biomagnification of mercury between 2 successive levels of the food chain. The FCM is determined using mercury concentration data in fish in a predator-prey relationship. Example: the FCM for trophic level 4 fish is the ratio of methylmercury in large TL4 fish to methylmercury in small TL3 fish.

A trophic level ratio (TLR) is the ratio of methylmercury concentrations in fish of different trophic levels, but is derived using data for fish in the same size classification. For example, an osprey may consume sunfish (TL3) and bass (TL4). A 350 mm sunfish, though, is too large to be preyed upon by an equivalently-sized smallmouth bass. Therefore, the ratio of mercury concentration in TL4 to TL3 fish eaten by osprey is termed a TLR rather than a FCM.

Table 4.4: Food Chain Multipliers and Trophic Level Ratios for Delta Wildlife Target Development

Translator	Value	Source	Relevant Wildlife Species [a]
Trophic Level Ratio (TLR)			
TLR 4/3	3.0	Ratio between existing MeHg concentrations in large TL4 fish (150-350 mm length) and large TL3 fish (150-350 mm length). Calculated from Delta-wide average fish tissue levels; see Appendix B.	Bald eagle, osprey
Food Chain Multipliers (FCM)			
FCM 4/3	8.1	Ratio between existing MeHg concentrations in large TL4 fish (150-350 mm length) and small TL3 fish (50-150 mm). Calculated from Delta-wide average fish tissue levels; see Appendix B.	River otter
FCM 3/2	5.7	Ratio between MeHg concentrations in large TL3 fish and small TL2 fish. From USFWS (2004) based on national averages.	Bald eagle, peregrine falcon
FCM piscivorous birds (FCM PB)	12.5	Ratio between MeHg in piscivorous bird tissue and in small TL3 prey fish. From USFWS (2003).	Bald eagle, peregrine falcon
FCM omnivorous birds (FCM OB)	10	Ratio between MeHg in omnivorous bird tissue and in small, TL2/3 prey fish and other aquatic organisms. From USFWS (2003).	Bald eagle, peregrine falcon

(a) Wildlife species for which the translator is used to determine safe tissue levels.

4.5.3.1 River Otter Safe Tissue Levels

To calculate the safe concentrations for otter, the safe concentrations in TL3 and TL4 fish need to be determined. In order to solve for these two variables using Equation 4.3, the TL4 fish concentration is expressed in terms of the TL3 fish concentration. River otters eat a wide range of prey sizes. Large fish in the otter diet likely prey on small fish that otter also eat. Therefore, the TL4 variable is expressed using the TL3 concentration and a food chain multiplier (FCM 4/3). From the Delta field data, staff determined that the methylmercury concentration in large TL4 fish is 8.1 times the concentration in small TL3 fish. Safe tissue levels in TL3 and TL4 fish for otter are determined by:

$$TDSL_{otter} = (\%\ dietTL_3 * TL3_{conc}) + (\%\ dietTL_4 * TL4_{conc})$$

Where: $TL4_{conc} = TL3_{conc} * FCM\ 4/3$

$$0.107\ mg/kg = (0.80 * TL3_{conc}) + (0.20 * 8.1 * TL3_{conc})$$

Solving for $TL3_{conc}$:

$$TL3_{conc} = 0.044\ mg\ MeHg/kg\ fish$$

$$TL4_{conc} = 0.044\ mg/kg * 8.1 = 0.36\ mg\ MeHg/kg\ fish$$

This equation produces safe levels of 0.04 and 0.36 mg/kg in small TL3 and large TL4 fish, respectively, which are shown in Table 4.3.

4.5.3.2 Osprey safe tissue levels

Safe methylmercury tissue levels for osprey are calculated like those for river otter, with the exception of the trophic level translator. Trophic level 3 and 4 fish eaten by osprey tend to be of similar sizes. Because there is not a food chain relationship between similarly sized fish, the osprey values are calculated using a trophic level ratio (TLR 4/3). On average in the Delta, methylmercury levels in large TL4 fish are 3.0 times the levels in large TL3 fish.

$$TDSL_{osprey} = (\%\ dietTL_3 * TL3_{conc}) + (\%\ dietTL_4 * TL4_{conc})$$

Where:

$$TL4_{conc} = TL3_{conc} * TLR\ 4/3$$

$$0.105\ mg/kg = (0.90 * TL3_{conc}) + (0.10 * 3.0 * TL3_{conc})$$

Solving for $TL3_{conc}$:

$$TL3_{conc} = 0.088\ mg\ MeHg/kg\ fish$$

$$TL4_{conc} = 0.088\ mg/kg * 3.0 = 0.26\ mg\ MeHg/kg\ fish$$

4.5.3.3 Bald Eagle Safe Tissue Levels

Calculation of methylmercury tissue levels for bald eagle is slightly more complicated because bald eagles consume omnivorous birds (OB), piscivorous birds (PB), and fish. The omnivorous birds of concern in the bald eagle diet feed on trophic level 2 aquatic prey (mostly invertebrates). To solve the equation, safe tissue concentrations in the other eagle prey types are expressed in terms of the lowest food chain level (TL2) common to all prey types (USFWS, 2004). To translate the TL2 concentration into the piscivorous bird safe level, staff used the food chain multiplier for TL3 small fish (FCM 3/2) and the food chain multiplier relating piscivorous birds and small TL3 fish (FCM PB). Like osprey, bald eagles tend to eat TL3 and TL4 fish of similar size, hence the use of the TL4/3 ratio.

$$TDSL_{bald\ eagle} = (\%\ dietTL_3 * TL3_{conc}) + (\%\ dietTL_4 * TL4_{conc}) + (\%diet_{OB} * OB_{conc}) + (\%diet_{PB} * PB_{conc})$$

Where:

$$TL3_{conc\ large\ fish} = TL2_{conc} * FCM\ 3/2$$

$$TL4_{conc\ large\ fish} = TL2_{conc} * FCM\ 3/2 * TL\ 4/3$$

$$OB_{conc} = TL2_{conc} * FCM\ OB$$

$$PB_{conc} = TL2_{conc} * FCM\ 3/2 * FCM\ PB$$

$$0.195\ mg/kg = (0.58*5.7*TL2_{conc}) + (0.13*5.7*3.0*TL2_{conc}) + (0.13*10*TL2_{conc}) + (0.05*5.7*12.5*TL2_{conc})$$

Solving for $TL2_{conc}$:

$$TL2_{conc} = 0.019\ mg\ MeHg/kg\ fish$$ *(not eaten by eagles; used to determine other safe levels)*

$$TL3_{conc\ large\ fish} = 0.019 * 5.7 = 0.11\ mg\ MeHg/kg\ fish$$

$$TL4_{conc\ large\ fish} = 0.019 * 5.7 * 3.0 = 0.31\ mg\ MeHg/kg\ fish$$

$$OB_{conc} = 0.019 * 10 = 0.19\ mg\ MeHg/kg\ omnivorous\ birds$$

$$PB_{conc} = 0.019 * 5.7 * 12.5 = 1.35\ mg\ MeHg/kg\ piscivorous\ birds$$

4.5.3.4 Peregrine Falcon Safe Tissue Levels

Peregrine falcons consume almost exclusively avian prey, some of which is aquatic-dependent. To solve for safe concentrations in omnivorous and piscivorous bird prey, these terms are expressed as functions of the lowest trophic level common to the birds' food web, which is TL2 aquatic prey (USFWS, 2004).

$$TDSL_{peregrine} = (\%diet_{OB} * OB_{conc}) + (\%diet_{PB} * PB_{conc})$$

Where:

$$OB_{conc} = TL2_{conc} * FCM\ OB$$

$$PB_{conc} = TL2_{conc} * FCM\ 3/2 * FCM\ PB$$

$$0.139\ mg/kg = (0.10 * 10 * TL2_{conc}) + (0.05 * 5.7 * 12.5 * TL2_{conc})$$

Solving for $TL2_{conc}$:

$TL2_{conc}$ = 0.030 mg MeHg/kg fish *(not eaten by peregrines; used to determine other safe levels)*

OB_{conc} = 0.030 * 10 = 0.30 mg MeHg/kg omnivorous birds

PB_{conc} = 0.030 * 5.7 * 12.5 = 2.2 mg MeHg/kg piscivorous birds

Note that the safe fish tissue levels in Table 4.3 are partially watershed-dependent and are specific to the Delta. The acceptable, average fish tissue concentrations for wildlife consuming from one trophic level will be consistent across different water bodies. This is because all of the parameters used to calculate the safe fish levels (species body weight, consumption rate and reference dose) were obtained from published literature and apply on a national or regional scale (Table 4.2). For species consuming fish from two trophic level classifications or piscivorous birds, translators (FCM or TLR) were used to calculate the safe concentrations in prey fish and piscivorous birds. These translators should be derived from site-specific data when possible and may differ between watersheds. For the Delta targets, the TLR and FCM between trophic level 4 and 3 fish were specific to the Delta. The FCMs for piscivorous birds, omnivorous birds and trophic level 3 fish were literature-derived average values.

Central Valley Water Board staff is not proposing safe tissue levels in piscivorous or omnivorous birds as TMDL targets. Data are lacking to compare safe levels in bird prey with existing conditions. By lowering methylmercury concentrations in fish and aquatic prey to safe levels shown in Table 4.3, staff anticipates that concentrations in birds feeding in the aquatic food web will decline to safe levels as well. In particular for peregrine falcon, the desired safe level in piscivorous birds is 2.2 mg/kg. Dividing the safe piscivorous bird level by 12.5 (FCM PB) results in a safe level in TL3 prey fish (150-350 mm length) of 0.17 mg/kg, which is above the proposed target for large TL3 fish.

Wildlife targets for TL3 and TL4 fish greater than 150 mm in length may be directly compared with targets developed to protect human consumers, as discussed in the following section. In Section 4.7, the wildlife and human targets that are trophic level and size-specific are incorporated into a single target based on largemouth bass that is protective of humans and all wildlife species of concern.

4.6 Human Health Targets

Numeric targets can be developed to protect humans in a manner analogous to targets for wildlife. A reference dose, average body weight and consumption rates are used along with Equations 4.1 and 4.3 to calculate safe fish tissue levels. In this section, the human health exposure parameters are discussed.

4.6.1 Acceptable Daily Intake Level

Central Valley Water Board staff used the USEPA RfD for methylmercury (USEPA, 2001) in Delta target calculations. The lowest level of methylmercury exposure that caused harm was determined in tests of neuropsychological function in children in the Faroe Islands and other sites exposed to methylmercury in fish. The USEPA divided the lowest effect level by ten to calculate a final RfD of 0.1 μg methylmercury/kg bwt/day (USEPA, 2001). The USEPA describes its RfD an exposure level that is not expected to cause harm over a lifetime of exposure on a daily basis. The ten-fold uncertainty factor accounts for differences in the extent to which individuals absorb, metabolize, and react to methylmercury. The USEPA RfD is applied to the general population.[17]

4.6.2 Body Weight & Consumption Rate

This report uses the USEPA's standard adult bodyweight of 70 kg. Using an average pregnant female bodyweight (65 or 67 kg) would have very little difference on the calculation of mercury targets in fish.

Consumption rate is the most difficult of the fish tissue target variables to select because human consumption is variable. The amount of methylmercury ingested is highly dependent on the amount of fish and the sizes and species of fish consumed. The preferred level of Delta fish consumption is bounded by the limited amount recommended in the existing fish advisory and the rate of a very high consumer. People could eat unlimited quantities of Delta fish if the fish mercury concentration was zero. Human health is best protected by both cleanup and education. Education is needed until the effects of mercury reduction are seen in fish tissue levels. During the TMDL implementation period, consumers should be encouraged to eat smaller fish and species with lower mercury concentrations.

A comprehensive survey of consumption of Delta fish has not been conducted. Thus, staff examined San Francisco Bay and national fish consumption studies, as well as several localized and pilot studies in the Delta, to develop Delta-specific consumption scenarios and ultimately recommend targets for human protection.

[17] "In the studies so far published on subtle neuropsychological effects in children, 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 (versus general population) RfD. This RfD is applicable to the lifetime daily exposure for all populations, including sensitive subgroups. It is not a developmental RfD per se, and its use is not restricted to pregnancy or developmental periods" *Water Quality Criterion for Methylmercury, Section 4-6* (USEPA, 2001).

The USEPA recommends default consumption rates for the general population and some subpopulations (USEPA, 2000a). Default consumption rates are derived from data collected nationwide as part of the 1994-96 USDA Continuing Survey of Food Intake by Individuals (CFSII). The USEPA reports rates separately for consumption of freshwater and marine fish. The USEPA recommends a fish intake rate of 17.5 g/day (about one 8-ounce uncooked fish meal every two weeks[18]) to protect the general population consuming freshwater and estuarine fish. This value represents the 90th percentile consumption rate for all survey participants, including those who do not eat fish. In selecting the 90th percentile, rather than the mean or median, the USEPA intended to recommend a consumption rate that is protective of the majority of the entire population. The USEPA recommended a consumption rate of 142.4 g/day (four to five 8-ounce, uncooked, portions per week) of local fish to represent anglers who use locally caught fish as a main source of protein. This value represents the 99th percentile consumption rate for all survey participants.

A detailed survey of consumption by anglers in San Francisco Bay was conducted in 1998 and 1999 (SFEI, 2000). The consumption rates for the 90th and 95th percentiles of anglers that were "consumers" (consumed Bay fish at least once prior to the interview) were 16 and 32 g/day, respectively. The San Francisco Bay Mercury TMDL selected the consumption rate for the 95th percentile of anglers (32 g/day) for calculation of the San Francisco Bay fish mercury target (0.2 mg/kg) to protect people who choose to eat San Francisco Bay fish on a regular basis (Johnson and Looker, 2004; SFBRWQCB, 2006).

California Department of Public Health staff interviewed members of communities thought to have high consumption rates (CDHS, 2004) and conducted several pilot fish consumption surveys in the Delta (CDHS, 2005 and 2006; Ujihara, 2006). From the interviews, CDPH learned that being able to safely eat Delta fish is important to many people. Members of all races and many ethnic groups fish in the Delta. Preferences for angling location, language spoken, and fish species are important for developing education and outreach programs.

The CDPH conducted small surveys of anglers in three parts of the Delta (CDHS, 2005 and 2006; Ujihara, 2006). Of boaters docking in Contra Costa County surveyed in 2005, 50% reported never eating Delta fish; 3% ate it more than once per week. Of boat and shore anglers on the Sacramento River between Rio Vista and the American River interviewed during salmon season in 2003, 17% ate Delta fish more than once per week. Shore anglers at two southern Delta and two San Joaquin River sites outside the Delta were interviewed in October/November 2005. Of the total respondents who ate any fish in the 30-day period prior to the survey, the geometric mean consumption rates were 22, 17, and 27 grams uncooked fish per day for locally caught, commercial, and total fish, respectively; these rates are less than one 8-ounce meal per week. Anglers were typically male. Many respondents in the Sacramento River and Delta/San Joaquin River angler surveys said that women and children in their households eat Delta fish.

[18] Although the target calculations use bodyweights and consumption rates for adult humans, the resulting fish tissue levels protect children as well. Children's bodyweights and smaller portion sizes can also be fitted into Equations 4.1 and 4.3. The OEHHA has published a table of sizes of typical meals of fish that correspond to smaller bodyweights (OEHHA, 1999). Children would only be at risk of mercury toxicity if they consumed more than the average portion for their body size.

A recent fish consumption and advisory awareness survey of low-income women at a WIC[19] clinic in Stockton found that 32% of the 500 survey participants ate Delta fish and 95% ate commercial fish (Silver *et al*., 2007). For participants who ate any fish in the 30-day period prior to the survey, the geometric mean consumption rates equaled 13, 33, and 35 grams uncooked fish per day for Delta, commercial, and total fish, respectively.[20] Cambodian, Asian/Pacific Islander, and African American participants had the highest mean consumption rates (24, 22, and 18 grams uncooked fish per day, respectively).

In 2005-2008, researchers from University of California Davis interviewed anglers and community members in the Delta about eating fish (Shilling, 2009). The study area included the Sacramento River between Rio Vista and the American River and the Sacramento Deep Water Ship Channel. The average and 95th percentile rates of consumption of locally caught fish were 11 and 52 g/day uncooked fish/day, respectively. Women and men ate fish at similar rates. Average consumption rates of locally caught fish were highest for Lao, African American, and Vietnamese participants.

4.6.3 Consumption of Fish from Various Trophic Levels & Sources

Species and size of fish as well as consumption rate affect methylmercury intake. It is difficult to estimate amounts of various species of sport fish that might be consumed from the Delta. Based on the CSFII national survey, the USEPA assumed that humans eat freshwater and estuarine fish from trophic levels two (3.8 g/day), three (8.0 g/day) and four (5.7 g/day) (USEPA, 2001). These rates are 21.7, 45.7, and 32.6% of the total 17.5 g/day, respectively. Trophic level 2 species, such as clams, crayfish, shrimp and shimofuri goby, are harvested from the Delta for human consumption (Appendix C). However, CDFG creel surveys (CDFG, 2000-2001) and anecdotal information provided by CDFG staff (Schroyer, 2003) indicate that many Delta anglers do not take home TL2 species. As described in Figure C.1 in Appendix C, the creel surveys indicate that Delta anglers may target an almost even mix of TL3 (American shad, salmon, sunfish, splittail) and TL4 (catfish and striped bass) fish in the Sacramento and Mokelumne Rivers subareas of the Delta, and primarily TL4 species (striped bass and catfish) throughout the rest of the Delta. Anecdotal information provided by CDFG staff (Schroyer, 2003) indicates that even in the rest of the Delta, many anglers take home a mix of TL3 and TL4 fish species. In the Delta consumption surveys described in previous paragraphs, anglers reported taking home catfish, striped bass, carp, bluegill, salmon, largemouth bass, crappie, sturgeon, and crayfish (CDHS, 2005 and 2006; Ujihara, 2006).

When evaluating potential fish tissue targets, staff considered five different tropic level distributions of locally caught fish (Table 4.5). Staff considered the TL2/3/4 mixture used by the USEPA for one distribution and Delta-specific information to develop four other distributions: 100% TL4, even mix of TL3 and 4, and an even mix of TL3 and 4 with small amounts of TL2 species (e.g., clams and shrimp).

[19] Special Supplemental Nutrition program for Women, Infants, and Children (WIC).

[20] This study reported consumption in grams of cooked fish. In order to compare the studies, Central Valley Water Board staff converted units of cooked fish to uncooked fish by multiplying by 1.25.

When determining safe levels of Delta fish consumption, staff also considered the intake of methylmercury from commercial fish (see definition of RSC in Section 4.4). Many fish consumers eat a combination of locally caught and commercially bought fish. Based on the national CFSII survey, the USEPA assumes an average consumption rate of commercial fish of 12.46 g/day, which results in an average daily intake of 0.027 µg methylmercury/kg bwt-day (USEPA, 2001). For people eating fish from commercial markets and the Delta, the safe intake level of methylmercury from Delta fish is the reference dose minus the methylmercury from commercial fish (0.1 µg/kg-day minus 0.027 µg/kg-day equals 0.073 µg/kg-day).[21]

4.6.4 Safe Rates of Consumption of Delta Fish

The USEPA issued a recommended criterion of 0.3 mg/kg methylmercury in locally caught fish consumed by humans (USEPA, 2001) [22]. The USEPA human health criterion was calculated using a default consumption rate of freshwater/estuarine fish of 17.5 g/day (about one meal every two weeks) and commercial (marine) fish of 12.46 g/day. The criterion assumed that humans eat freshwater and estuarine fish from TL2 (21.7%), TL3 (45.7%) and TL4 (32.6%). However, the USEPA's Water Quality Criterion report noted that the criterion can be adjusted on a site-specific basis to reflect regional or local consumption patterns and/or specific populations of concern. These include the consumption rates of local fish and the RSC estimate. For example, the San Francisco Bay mercury fish tissue objective of 0.2 mg/kg was calculated using a consumption rate of 32 g/day (about one meal per week) derived from a San Francisco Bay consumption survey. The San Francisco Bay objective is applied to the average mercury concentration in the five most commonly consumed Bay fish species: striped bass, California halibut, jacksmelt, white sturgeon, and white croaker (three TL4 species and two TL3 fish species; SFBRWQCB, 2006).

In the absence of Delta-specific consumption rates, the USEPA default consumption rate (17.5 g/day), San Francisco Bay consumption rate (32 g/day), and USEPA recommended consumption rate for anglers whose main source of protein is from locally caught fish (142.4 g/day) were used in Equation 4.1 to estimate the safe methylmercury level in the total diet for humans consuming Delta fish (Table 4.5). In addition, scenarios were developed for anglers who consume Delta and commercial fish, and for anglers who consume only Delta fish. For each of the total diet safe levels associated with the different consumption rates, different distributions of locally caught fish were considered. Because some Delta consumers eat TL2 species, two scenarios assume Delta consumers eat small proportions of TL2 species.

Equation 4.3 was used to develop safe levels for each trophic level of Delta fish. In order to solve Equation 4.3 for the desired concentrations in TL2, TL3 and TL4 biota, concentrations in the higher trophic levels are put in terms of the concentration in the lowest trophic level.

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[21] Most commercial fish do not come from the Delta. The most popular fish and seafood bought in commercial markets are marine species such as scallops, shrimp, and tuna. The average consumption rate of marine fish reported by all respondents in the national CFSII survey was 12.46 g/day (three meals every two months; USEPA, 2001). The average concentration of methylmercury in commercial species weighted by frequency of consumption is 0.16 mg/kg (USEPA, 2001)

[22] The USEPA rounded from 0.288 mg/kg to 0.3 mg/kg for use as its recommended methylmercury criterion. Central Valley Water Board staff's calculations throughout the rest of this report are rounded to two decimal places, e.g., 0.29 mg/kg.

Equation 4.3 is then rearranged to solve for the lowest trophic level concentration. In order to express the concentration in a higher trophic level, trophic level ratios were used. The TLRs used in the calculation of Delta human targets are shown in Table 4.6. Existing Delta fish concentration data were used to develop the ratios. The following example illustrates how the trophic level fish targets were developed for Scenario A.1 in Table 4.5 using Equations 4.1 and 4.3.

Per Equation 4.1:

$$\text{Safe MeHg in total diet of Delta fish} = \frac{\text{(Human RfD - Relative source contribution) * Body weight}}{\text{Consumption rate}}$$

$$0.29\ \text{mg/kg} = \frac{0.073\ \mu\text{g MeHg/kg-day} * 70\ \text{kg}}{17.5\ \text{g/day}}$$

Per Equation 4.3:

$$0.29\ \text{mg/kg} = (\%\ \text{dietTL}_2 * \text{TL3}_{conc}) + (\%\ \text{dietTL}_3 * \text{TL3}_{conc}) + (\%\ \text{dietTL}_4 * \text{TL4}_{conc})$$

Where: $\text{TL3}_{conc} = \text{TL2}_{conc} * \text{TLR } 3/2$

$\text{TL4}_{conc} = \text{TL2}_{conc} * \text{TLR } 3/2 * \text{TLR } 4/3$

$$0.29\ \text{mg/kg} = (21\% * \text{TL2}_{conc}) + (46\% * \text{TL2}_{conc} * 4.5) + (33\% * \text{TL2}_{conc} * 4.5 * 2.9)$$

Solving for $TL2_{conc}$*:*

TL2_{conc} = 0.30 / (0.21 + (0.45*4.5) +(0.33*4.5*2.9)) = 0.046 mg/kg in shrimp & clams

TL3_{conc} = 0.046 mg/kg * 4.5 = 0.20 mg/kg in 150-500 mm fish

TL4_{conc} = 0.046 mg/kg * 4.5 * 2.9 = 0.45 mg/kg in 150-500 mm fish

The highlighted safe levels for TL3 and TL4 fish in Scenarios A.1, A.4, B.4 and E.3 are evaluated as fish tissue objective alternatives in Chapter 3 of the draft Basin Plan Amendment staff report. As indicated by Table 4.5, potential safe levels of mercury in large Delta TL4 fish range from 0.05 to 0.80 mg/kg. Safe methylmercury concentrations can be higher when consumers of Delta fish do not eat commercial fish. However, in interviews of local community based groups and pilot surveys, most respondents who eat Delta fish consume commercial fish as well (CDHS, 2004; Silver 2007; and Ujihara, 2006). Staff therefore narrowed the options for further consideration by assuming Delta fish consumers eat commercial fish unless consumers are highly dependent on Delta fish (Scenario E).

Including small amounts of TL2 species into the diet distribution (Scenarios A.2, A.3, B.2, and B.3) makes little difference in the safe methylmercury concentrations in TL3 and TL4 fish, relative to an even mix of just TL3 and TL4 fish. To protect the many Delta anglers who likely do not eat TL2 species, staff proceeded with consideration of TL3 and 4 fish only.

To further assess the feasibility of attaining the targets, staff compared them to regional background conditions defined by a recent study by the USEPA and Oregon State University (Peterson *et al.*, 2007). This study included the collection and analysis of 2,707 large TL3 and TL4 fish from 626 streams and river segments in the western United States, including California, using a probability design. The purpose of the study was to assess the distribution of mercury in fish across the western United States. Central Valley Water Board staff evaluated the study results in terms of the existing fish mercury levels in the Delta and alternative fish tissue targets (Foe, 2007).

Only about 1 to 3% of the waterways evaluated by the regional study had fish mercury concentrations higher than those observed in the Mokelumne/Cosumnes subarea of the Delta. Likewise, fish mercury concentrations in the Sacramento, San Joaquin, and Yolo Bypass subareas were in the top 20 to 25% of fish mercury concentrations observed throughout the western United States. This confirms that Delta fish have elevated concentrations in comparison to regional background levels and suggests that the Delta and its tributary watersheds contain mercury sources in addition to atmospheric deposition, e.g., abandoned mines and sites where the mercury is efficiently converted to methylmercury that bioaccumulates in the aquatic food web (Foe, 2007). Of the sampled waterways in the western United States, none supported a fish population with mercury concentrations as low as Scenario E.3 (0.05 mg/kg in large TL4 fish) (Peterson *et al.*, 2007; Foe, 2007). Therefore, this target may not be attainable. In contrast, about 30% to 40% of the sampled waterways supported a fish population with mercury concentrations lower than Scenarios A.1, A.4, and B.4, suggesting that these scenarios may be attainable with implementation of a vigorous control program.

As discussed in the draft Basin Plan Amendment staff report, the TL3 and TL4 targets produced by Scenario B.4 of 0.08 mg/kg and 0.24 mg/kg, respectively, are recommended by Central Valley Water Board staff for the protection of humans for several reasons:

- They fully protect wildlife species consume large fish, including threatened and endangered species as required by the Endangered Species Act.
- They reasonably protect people who eat Delta fish by safely allowing the consumption of one eight-ounce meal per week of Delta fish, a consumption rate greater than the USEPA default rate used in Scenarios A and C. These objectives are therefore more protective of people who by custom, need, or enjoyment, more frequently eat Delta fish.
- They incorporate local consumption patterns, which show that Delta anglers commonly target fish like salmon (TL3) and striped bass (TL4).
- They are consistent with the fish tissue objectives approved by the State Water Board for San Francisco Bay (SFBRWQCB, 2006; SWRCB, 2007). Like the Scenario B.4 targets, the methylmercury objective recommended for the Bay is based on protecting people who eat 32 g/day of local fish. Scenario B.4 takes into consideration that people, fish-eating wildlife and their prey (e.g., anadromous species) travel between the Delta and San Francisco Bay.
- They are attainable because they are not less than background fish mercury levels in the western United States and they can be reliably measured (given current analytical methods for water and fish; see Section 5.2 in Chapter 5).

These targets are carried forward throughout the rest of this report for use in the food web evaluation, linkage analysis and development of methylmercury source allocations.

Table 4.5: Safe Concentrations of Methylmercury in Delta Fish by Trophic Level (TL) to Protect Humans Calculated Using Varying Assumptions about Consumption Rates and Trophic Level Distribution.

Scenario	Body Weight (kg)	Acceptable Daily Delta Fish MeHg Intake Level (µg/kg-day) (a)	Total Consumption Rate of Delta Fish (g/day) (b)	Safe MeHg Level in Total Diet of Delta Fish (mg/kg) (c)	Distribution of Locally Caught Fish by TL			Safe Concentration of MeHg in Fish by TL (mg/kg) (d)		
					TL2	TL3	TL4	TL2	TL3	TL4
For people eating commercial and Delta fish:										
A.1	70	0.073	17.5	0.29	21.7%	45.7%	32.6%	0.04	**0.20**	**0.58**
A.2					10%	45%	45%	0.04	0.16	0.47
A.3					5.0%	47.5%	47.5%	0.03	0.16	0.45
A.4					---	50%	50%		0.15	0.43
A.5					---	---	100%			**0.29**
B.1	70	0.073	32	0.16	21.7%	45.7%	32.6%	0.02	0.11	0.32
B.2					10%	45%	45%	0.02	0.09	0.26
B.3					5.0%	47.5%	47.5%	0.02	0.09	0.25
B.4					---	50%	50%		**0.08**	**0.24**
B.5					---	---	100%			0.16
For people eating only Delta fish:										
C.1	70	0.1	17.5	0.40	21.7%	45.7%	32.6%	0.06	0.28	0.80
C.2					---	50%	50%		0.21	0.59
C.3					---	---	100%			0.40
D.1	70	0.1	32	0.22	21.7%	45.7%	32.6%	0.03	0.15	0.44
D.2					---	50%	50%		0.11	0.33
D.3					---	---	100%			0.22
E.1	70	0.1	142.4	0.05	21.7%	45.7%	32.6%	0.01	0.03	0.10
E.2					---	50%	50%		0.03	0.07
E.3					---	---	100%			**0.05**

(a) For people eating fish from commercial markets and the Delta, the safe intake level of methylmercury from Delta fish is the USEPA reference dose minus the methylmercury from commercial fish (0.1 µg/kg-day minus 0.027 µg/kg-day = 0.073 µg/kg-day). Scenarios C through E assume no commercial fish are consumed.

(b) The USEPA human health criterion was calculated using a default consumption rate of freshwater/estuarine fish of 17.5 g/day and of commercial (marine) fish of 12.46 g/day, as derived from national dietary surveys (USEPA, 2001). The criterion assumed that humans eat freshwater and estuarine fish from TL2 (21.7%), TL3 (45.7%) and TL4 (32.6%).

(c) The USEPA criterion calculations yielded a methylmercury value of 0.288 mg methylmercury/kg fish, which the USEPA rounded to one significant digit. The Region 2 San Francisco Bay Mercury TMDL target calculations yielded a methylmercury value of 0.16 mg methylmercury/kg fish, which Region 2 also rounded to one significant digit in the San Francisco Bay Mercury TMDL report (Johnson and Looker, 2004).

(d) Values were calculated using Equation 4.3 and trophic level ratios presented in Table 4.6. Values were rounded to two decimal places. The highlighted targets (Scenarios A.1, A.4, B.4 and E.3) are evaluated as fish tissue objective alternatives in the draft Basin Plan Amendment staff report. The TL3 and TL4 targets produced by Scenario B.4 are recommended for the protection of humans that consume fish from throughout the Delta and are carried forward throughout the rest of this report for use in the linkage analysis and development of allocations.

Table 4.6: Trophic Level Ratios for Delta Human Target Development

Translator	Value	Source
TLR 4/3	2.9	Ratio between existing MeHg concentrations in large TL4 fish (150 mm [or legal catch limit] to 500 mm length) and large TL3 fish (150 mm [or legal catch limit] to 500 mm length). Calculated from Delta-wide average fish tissue levels; see Appendix B.
TLR 3/2	4.5	Ratio between existing MeHg concentrations in large TL3 fish (150-500 mm length) and TL2 species potentially consumed by humans (shrimp and clams). Calculated from Delta-wide average fish tissue levels; see Appendices B, C and K.

4.7 Trophic Level Food Group Evaluation

As noted in the previous section, Central Valley Water Board staff recommends targets of 0.08 and 0.24 mg/kg in large TL3 and TL4 fish, respectively, for the protection of humans that consume fish from throughout the Delta. In this section, the relationships between methylmercury concentrations in large TL4 fish and the other trophic level food groups are examined. The purpose of this analysis is to determine whether consistent relationships might exist between the assemblages of fish and, if so, whether it might be possible to describe safe mercury ingestion rates for humans and wildlife species in terms of large TL4 fish. This analysis enables staff to determine whether a water quality objective based on methylmercury in large fish developed for the protection of humans may or may not be protective of wildlife species that consume smaller or lower trophic level fish.

4.7.1 Data Used in Trophic Level Food Group Evaluation

Mercury concentrations for each trophic level food group sampled in the Delta are presented in Appendix K and summarized in Table 4.7. Values presented are average concentrations, weighted by the number of individual fish in composite samples. The trophic level food group concentrations are the result of analyzing 1,048 composite samples of 4,578 fish from 23 species in the Delta (Table B.2 and B.3 in Appendix B and Appendix K). Figure 4.1 illustrates the fish sampling locations used in the trophic level food group evaluation. The sampling was conducted by CDFG, SFEI, University of California, Davis, the Toxic Substances Monitoring Program, and the Sacramento River Watershed Program (Davis *et al.*, 2000; Davis *et al*., 2003; Slotton *et al.*, 2003; LWA, 2003; SWRCB-DWQ, 2002).

The data for each food group were assembled after considering four general rules. First, the data were restricted to samples collected between 1998 and 2001, the period with the most comprehensive sampling across the Delta. Second, migratory species (salmon, American shad, steelhead, sturgeon, and striped bass) were excluded. These species likely do not reside year-round at the locations in the Delta where they were caught and their tissue mercury levels may not show a positive relationship with the mercury levels in resident animals. In addition, data for migratory species are not available for all Delta subareas, precluding an analysis to determine whether such a relationship might exist. A review of data available for several commercial species (striped bass, salmon, blackfish and crayfish) is provided in Appendix C.[23] Third, fish samples with lengths greater than 500 mm were not included. Data for fish larger than 500 mm are available for only some subareas. Capping the size at 500 mm allows comparable data for all Delta subareas. Finally, only fish fillet data were used in the human and eagle trophic level food group analysis. Humans typically consume fish fillets, while wildlife species, including eagles, eat whole fish. However, all the data for large fish typically consumed by eagles and other large wildlife species are from fillet samples, making it necessary to use fillet information for these species.[24] Whole fish data were used for the smaller wildlife species food groups.

Of the eight Delta subareas identified in Section 2.2.2 and Figure 2.2, three of the subareas were not included in the trophic level food group evaluation due to inadequate information. No fish were sampled from the Marsh Creek subarea between 1998 and 2001. In addition, small fish were sampled throughout the Yolo Bypass-South subarea between 1998 and 2001, but large fish were sampled only in the southernmost area; hence, the mercury levels in the trophic level food groups are not geospatially comparable. The only fish sampling conducted in the Yolo Bypass-North subarea took place in Greens Lake, which is not considered representative of the entire subarea. In addition, only large TL4 fish were sampled; no small fish were sampled.

Table 4.8 provides a comparison of the average mercury concentrations for each trophic level food group sampled in the Delta (Table 4.7) to the recommended targets for the species with the lowest safe fish methylmercury levels within each trophic level food group. The comparison indicates that the recommended targets for wildlife protection are already met in the Central and West Delta subareas. In addition, the comparison indicates that greater reductions may be required to achieve the recommended target for large TL4 fish developed for human protection than for the recommended targets for smaller and lower trophic level fish developed for wildlife protection. The following section describes a more direct method for comparing the level of protection provided by the different trophic level food group targets.

4.7.2 Trophic Level Food Group Comparisons

Regressions between methylmercury concentrations in large TL4 fish and the other TL food groups are presented in Figure 4.2. The relationships were evaluated using linear, exponential, logarithmic, and power curves; in each case the type of curve that provided the highest R^2 value was selected. All of the correlations were statistically significant ($P<0.05$ or less). The regressions demonstrate that there are predictable relationships between mercury concentrations in large TL4 fish and the other trophic level food groups in the Delta.

[23] Methylmercury concentrations in salmon and striped bass are important to human risk assessment because people frequently attempt to catch these two species. Average mercury concentrations in striped bass are similar to mercury levels in largemouth bass. The available mercury data for salmon indicate that their tissue concentrations are much lower that the mercury levels in bass (0.04 to 0.12 mg/kg). See Appendix C for more information about striped bass and salmon.

[24] Researchers in New York found that concentrations in whole body and muscle of large TL3 and TL4 fish were not significantly different (Becker and Bigham, 1995), suggesting that it is appropriate to use fillet data to evaluate exposure to wildlife species.

Table 4.9 presents the predicted safe dietary mercury concentrations for each target species in terms of large TL4 fish calculated from the regression equations in Figure 4.2. The recommended target of 0.24 mg/kg in large TL4 fish developed for the protection of humans is lower than the corresponding safe large TL4 fish mercury concentrations predicted for the other TL food groups, which ranged from 0.30 mg/kg for Western grebe to 1.12 mg/kg for Western snowy plover. This indicates that the recommended targets for large TL3 and TL4 fish developed for protection of humans are most likely protective of wildlife species that consume smaller or lower trophic level fish. In other words, reductions in methylmercury levels needed to achieve the recommended targets for large TL3 and TL4 fish are expected to produce reductions in smaller fish sufficient to fully protect wildlife species. To ensure that wildlife species dining only on small fish are protected, staff proposes an additional target of 0.03 mg/kg methylmercury in TL2 and 3 fish less than 50 mm in length. This target represents the safe level for prey consumed by the California least tern, a piscivorous species listed by the federal government as endangered. As shown in Table 4.9, such a target for small fish also would protect the Western snowy plover.

Table 4.7: Mercury Concentrations in Trophic Level Food Groups Sampled in the Delta

Trophic Level Food Group	Hg Concentrations (mg/kg) by Delta Subarea [a]				
	Central Delta	Mokelumne River	Sacramento River	San Joaquin River	West Delta
TL4 Fish (150-500 mm)	0.26	0.92	0.56	0.50	0.32
TL3 Fish (150-500 mm)	0.08	0.28	0.21	0.11	0.11
TL4 Fish (150-350 mm)	0.20	0.75	0.46	0.42	0.24
TL3 Fish (150-350 mm)	0.08	0.29	0.17	0.12	0.08
TL3 Fish (50-150 mm)	0.03	0.09	0.04	0.04	0.03
TL3 Fish (<50 mm)	0.02	0.07	0.03	0.04	0.03

(a) The trophic level food group mercury levels are weighted averages of mercury levels for resident fish within each food group collected in each Delta subarea between 1998 and 2001. These food groups correspond to the proposed numeric targets developed earlier in Chapter 4. Weighted average mercury concentration is based on the number of fish in the composite samples analyzed, rather than the number of samples.

Table 4.8: Percent Reductions in Fish Methylmercury Levels Needed to Meet Numeric Targets

Trophic Level Food Group	Target Species [a]	Target (mg/kg)	Delta Subareas				
			Central Delta	Mokelumne River	Sacramento River	San Joaquin River	West Delta
TL4 Fish (150-500 mm)	Human	0.24	8%	74%	57%	52%	25%
TL3 Fish (150-500 mm)	Human	0.08	0%	71%	62%	27%	27%
TL4 Fish (150-350 mm)	Osprey	0.26	0%	65%	43%	38%	0%
TL3 Fish (150-350 mm)	Grebe	0.08	0%	72%	53%	33%	0%
TL3 Fish (50-150 mm)	Kingfisher	0.05	0%	44%	0%	0%	0%
TL3 Fish (<50 mm)	Least Tern	0.03	0%	57%	0%	25%	0%

(a) Only the recommended targets for the wildlife species with the lowest safe methylmercury concentrations in fish diet (Table 4.3) within each trophic level food group are evaluated. The proposed large TL3 and TL4 fish targets for human protection are lower than the targets proposed for protection of eagles.

Table 4.9: Predicted Safe Concentrations of Methylmercury in 150-500 mm TL4 Fish and Standard 350-mm Largemouth Bass Corresponding to Trophic Level Food Group (TLFG) Targets for the Protection of Piscivorous Species.

Trophic Level Food Group / Species	TLFG Target (mg/kg) [(a)]	Predicted 150-500 mm TL4 Fish Safe Level (mg/kg)	Predicted Standard 350-mm Largemouth Bass Safe Level (mg/kg) [(b)]
TL4 Fish (150-500 mm)			
Human	0.24	[(c)]	0.28
Bald eagle	0.31	[(c)]	0.36
TL3 Fish (150-500 mm)			
Human	0.08	0.24	0.24
Bald eagle	0.11	0.37	0.43
TL4 Fish (150-350 mm)			
Osprey	0.26	0.33	0.36
River otter	0.36	0.45	0.57
TL3 Fish (150-350 mm)			
Western grebe	0.08	0.30	0.31
Common merganser	0.09	0.35	0.38
Osprey	0.09	0.35	0.38
TL3 Fish (50-150 mm)			
Kingfisher	0.05	0.62	0.73
Mink	0.08	0.90	1.06
River otter	0.04	0.50	0.57
Double-crested cormorant	0.09	0.96	1.15
TL3 (<50 mm)			
California least tern	0.03	0.38	0.42
Western snowy plover	0.10	1.12	1.34

(a) The TLFG targets developed for bald eagle, osprey and river otter were developed using site-specific TLRs and/or FCMs combined with information provided in published literature. All other TLFG targets were entirely developed using information provided in published literature.

(b) The calculation and purpose of the standard 350-mm largemouth bass mercury concentrations are described in the following section (Section 4.8).

(c) The TL4 Goals are same as the TLFG Targets for human and eagle protection.

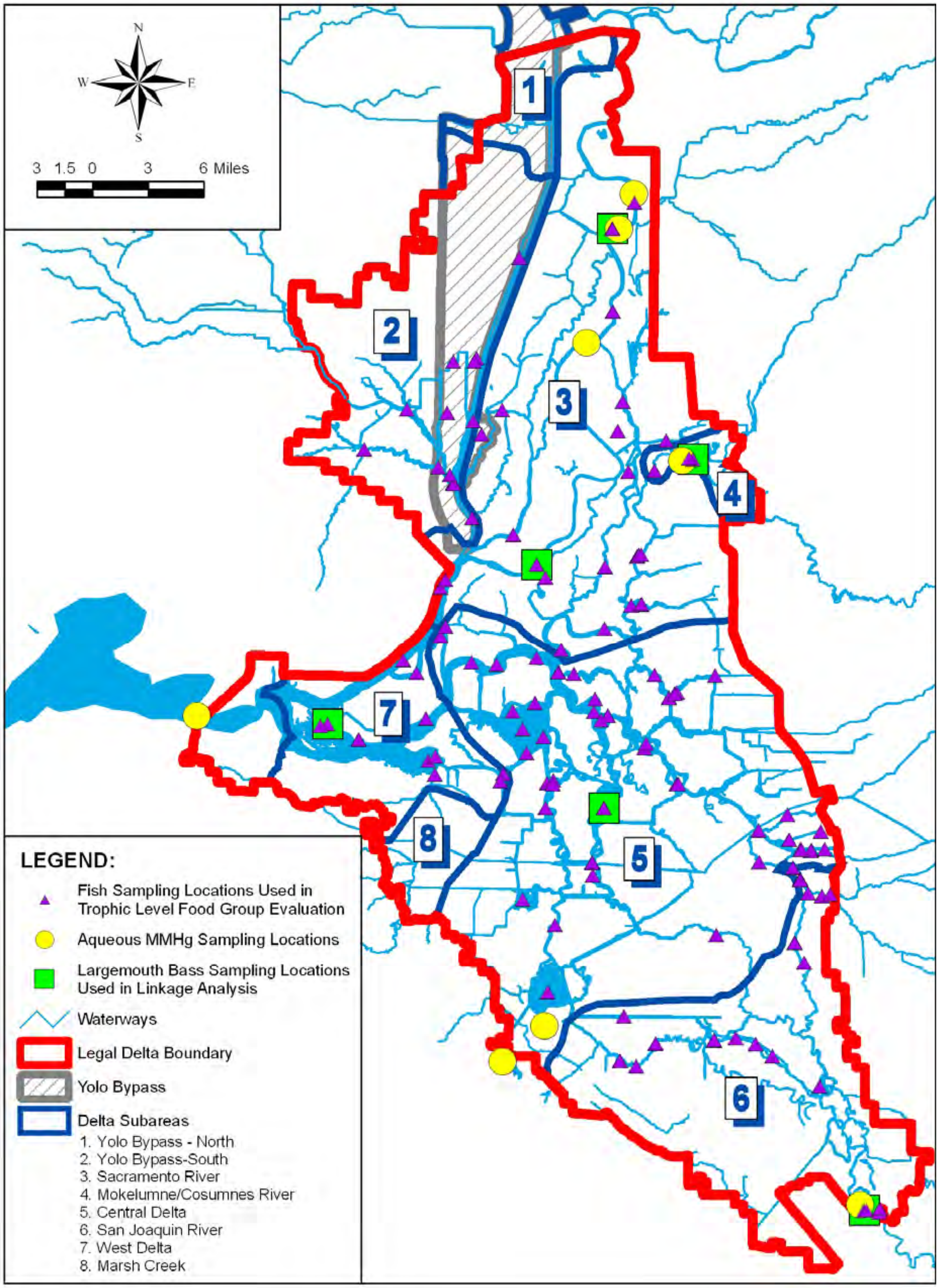

Figure 4.1: Fish and Water Sampling Locations Included in the Trophic Level Food Group and Largemouth Bass Evaluations.

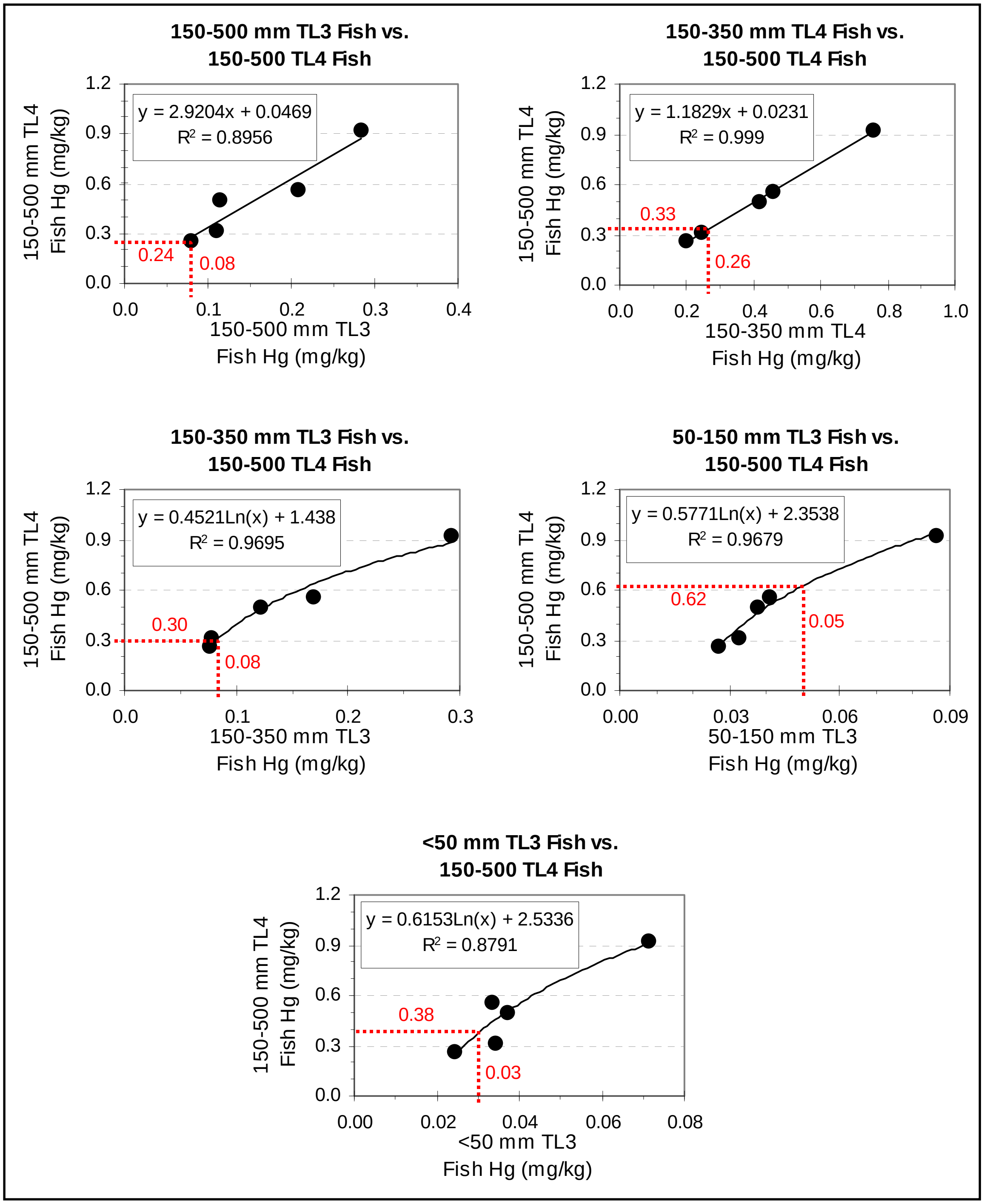

Figure 4.2: Comparison of Methylmercury Concentrations in Large (150-500 mm) TL4 Fish and Other Trophic Level (TL) Food Groups. The regressions are used to predict safe diets for target species listed in Table 4.9 in terms of large TL4 fish.

4.8 Largemouth Bass Evaluation

A goal of the TMDL is to link target methylmercury concentrations in fish to methylmercury concentrations in water to develop a goal for aqueous methylmercury that could then be used in development of an implementation plan. Chapter 5 (Linkage Analysis) describes the relationships between methylmercury in water and in largemouth bass in the Delta. Largemouth bass were selected for the linkage analysis for several reasons. Largemouth bass are a good bioindicator species. In addition, only largemouth bass data are available for the same sampling period and locations as the methylmercury water data (Figure 4.1). Largemouth bass, however, constitute only a portion of the diet of some of the human and wildlife consumers of Delta fish. The methylmercury targets determined above assume that humans and wildlife species consume a variety of sizes and species of fish from the Delta. In this section, the relationships between methylmercury concentrations in largemouth bass and the trophic level food groups were examined so that an implementation goal could be developed in terms of largemouth bass and, ultimately, linked to aqueous methylmercury.

Most of the information on mercury concentrations in the various trophic level food groups in the Delta was collected as species-specific composite samples between 1998 and 2001. Therefore, the largemouth bass evaluation was conducted in four parts. First, the methylmercury concentrations in largemouth bass of a standard size were estimated for each Delta subarea using the relationships between length and methylmercury tissue concentration[25] in samples collected in 2000. Second, correlations were run between standard 350-mm largemouth bass collected in 2000 and average concentrations of 300-400 mm largemouth bass (composite and individual samples) collected between 1998 and 2000. The year 2000 is significant because (1) aqueous methylmercury sampling began in March 2000 and (2) largemouth bass sampling adequate for the length/concentration regressions took place only in September/October 2000. The monthly March-October 2000 subset of the aqueous data has the greatest overlap with the lifespan of the largemouth bass sampled in September/October 2000. As these correlations were highly significant, the third step was to examine correlations between mercury concentrations in standard 350-mm largemouth bass and composites of all trophic level food groups collected in the Delta between 1998 and 2001. The purpose of this analysis was to determine whether consistent relationships might exist between the different assemblages of fish and, if so, whether it might be possible to describe safe mercury ingestion rates for humans and wildlife species in terms of the methylmercury concentration in a standard 350-mm largemouth bass. The final step was to determine a safe methylmercury concentration for each species in terms of the methylmercury concentration in 350-mm largemouth bass (Table 4.9).

[25] Determining the methylmercury concentration in a specific or "standard" size fish is a typical method of data analysis that allows comparison between sites and years. For largemouth bass from one site or subarea, mercury concentration is well correlated with length (Davis *et al*., 2003; data in Figure 4.3 in this report). This correlation is also useful in monitoring, as concentrations in fish in a range of lengths can be used to predict the concentration in a standard size. Hereafter, the mercury concentration in a "standard 350 mm largemouth bass" refers to the concentration obtained through a regression analysis as in Figure 4.3.

4.8.1 Largemouth Bass Standardization

The methylmercury content of a standard 350-mm length largemouth bass was determined at all sites where both water and fish tissue data were available (Figure 4.1) by regressing fish length against mercury body burden (Figure 4.3). Appendix K provides the concentration and length data for largemouth bass sampled in the Delta. Table 4.10 presents the predicted mercury values for 350 mm bass at each location where both water and fish tissue data were available. The predicted mercury concentration in standard 350 mm largemouth bass varied by a factor of five across the Delta (0.19 mg/kg in the Central Delta to 1.04 mg/kg in the Mokelumne River). Mercury concentration in a standard length 350 mm largemouth bass was selected because the length is near the middle of the size range collected at each site and therefore maximizes the predictive capability of the regression (Davis *et al*., 2003). Three hundred and fifty mm is slightly larger than CDFG's legal size limit of 305 mm (12 inches). A 350 mm bass is three to five years old (Schaffter, 1998; Moyle, 2002).

4.8.2 Correlations between Standard 350 mm and All Largemouth Bass Data

Figure 4.4 presents the regression between mercury levels in standard 350-mm largemouth bass collected in year 2000 and weighted-average concentrations in 300-400 mm largemouth bass collected between 1998 and 2000 in five delta subareas[26] (Table 4.10). Each data point represents one subarea. The correlation is statistically significant (P<0.01) and has a slope of 0.8, suggesting that mercury concentrations do not vary appreciably between the two groups. The results suggest that year 2000 standard 350-mm bass mercury levels are representative of mercury concentrations in largemouth bass collected between 1998 and 2000.

4.8.3 Largemouth Bass/Trophic Level Food Group Comparisons

Regressions between mercury concentrations in standard 350-mm largemouth bass and TL3 and TL4 food groups are presented in Figure 4.5. The purpose of this analysis was to determine whether consistent relationships might exist between the different assemblages of fish and, if so, whether it might be possible to describe safe mercury ingestion rates for wildlife species and humans in terms of the mercury concentration in a standard 350-mm largemouth bass. The relationships were evaluated using linear, exponential, logarithmic, and power curves; in each but one case the type of curve that provided the highest R^2 value was selected.[27] All of the correlations were statistically significant (P<0.05 or less). The regressions

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[26] Data collected in 1998-2000 contained individual and composite samples. Mercury concentrations in the composite samples were weighted by number of individual fish in the composite and then averaged with individual results.

[27] A logarithmic curve best fits the points comparing standard 350-mm largemouth bass mercury concentrations to 150-500 mm TL4 fish (Figure 4.3). However, the curve intercepts the x-axis well above zero, preventing the prediction of standard largemouth bass mercury concentrations that corresponds to the range of alternative large TL4 fish mercury targets developed for human protection (0.58, 0.29, 0.24 and 0.05 mg/kg). This is also true of a linear curve: it intercepts the x-axis above zero. Therefore, a linear equation with the intercept set to zero was used to estimate standard 350-mm largemouth bass mercury concentrations that correspond to the preferred and alternative large TL4 fish targets. All three regressions are statistically significant (P<0.01). Use of either the linear or logarithmic curves to predict safe levels for largemouth bass that correspond to the TL4 target alternatives has additional uncertainty because two of the alternatives (0.24 and 0.05 mg/kg) are lower than the lowest of observed values (0.26 mg/kg in the Central Delta subarea) upon which the curves are based.

demonstrate that there are predictable relationships between mercury concentrations in standard 350-mm largemouth bass and all trophic level food groups in the Delta.

Table 4.9 presents the predicted safe dietary mercury concentrations for each TLFG target in terms of standard 350-mm bass. The safe largemouth bass mercury levels were calculated from the regression equations in Figure 4.5. The lowest largemouth bass mercury value (0.24 mg/kg) corresponds to 0.08 mg/kg in 150-500 mm TL3 fish. This is the most conservative of all the calculated largemouth bass safe levels and, if attained, should fully protect all listed beneficial uses in the Delta. Staff recommends that **0.24 mg/kg, wet weight, in a standard 350-mm largemouth bass** be used as an **implementation goal** in the linkage analysis (Chapter 5) and determination of methylmercury allocations (Chapter 8).

As described in Tables 4.8 and 4.11, percent reductions in fish methylmercury levels ranging between 0 and 77% will be needed to meet the recommended numeric targets for large and small TL3 and TL4 fish and the implementation goal for standard 350-mm largemouth bass in the different Delta subareas. Staff expects that when methylmercury concentrations in largemouth bass reach the recommended implementation goal for standard 350-mm largemouth bass, then concentrations in other aquatic organisms also will have declined sufficiently to protect human and wildlife consumers. Monitoring should be conducted in all trophic level food groups at that time to verify that the expected decreases have occurred.

Key points and options to consider for the numeric targets are listed after Figure 4.5.

Table 4.10: Mercury Concentrations in Standard 350-mm and 300-400 mm Largemouth Bass

	Hg Concentrations (mg/kg) by Delta Subarea				
	Central Delta	Mokelumne River	Sacramento River	San Joaquin River	West Delta
Year 2000 Standard 350-mm largemouth bass collected in September/October 2000 [(a)]	0.19	1.04	0.72	0.68	0.31
300-400 mm largemouth bass collected between 1998 and 2000 [(b)]	0.31	0.94	0.76	0.64	0.30

(a) The standard 350-mm largemouth bass mercury concentrations are predicted values derived using the regressions in Figure 4.3.
(b) The values for the 300-400 mm bass are weighted-average concentrations in 300-400 mm largemouth bass collected between 1998 and 2000 from multiple locations within each of the five delta subareas.

Table 4.11: Percent Reductions in Standard 350-mm Largemouth Bass Methylmercury Levels Needed to Meet the Recommended Implementation Goal of 0.24 mg/kg in Each Delta Subarea.

Central Delta	Mokelumne River	Sacramento River	San Joaquin River	West Delta
0%	77%	67%	65%	23%

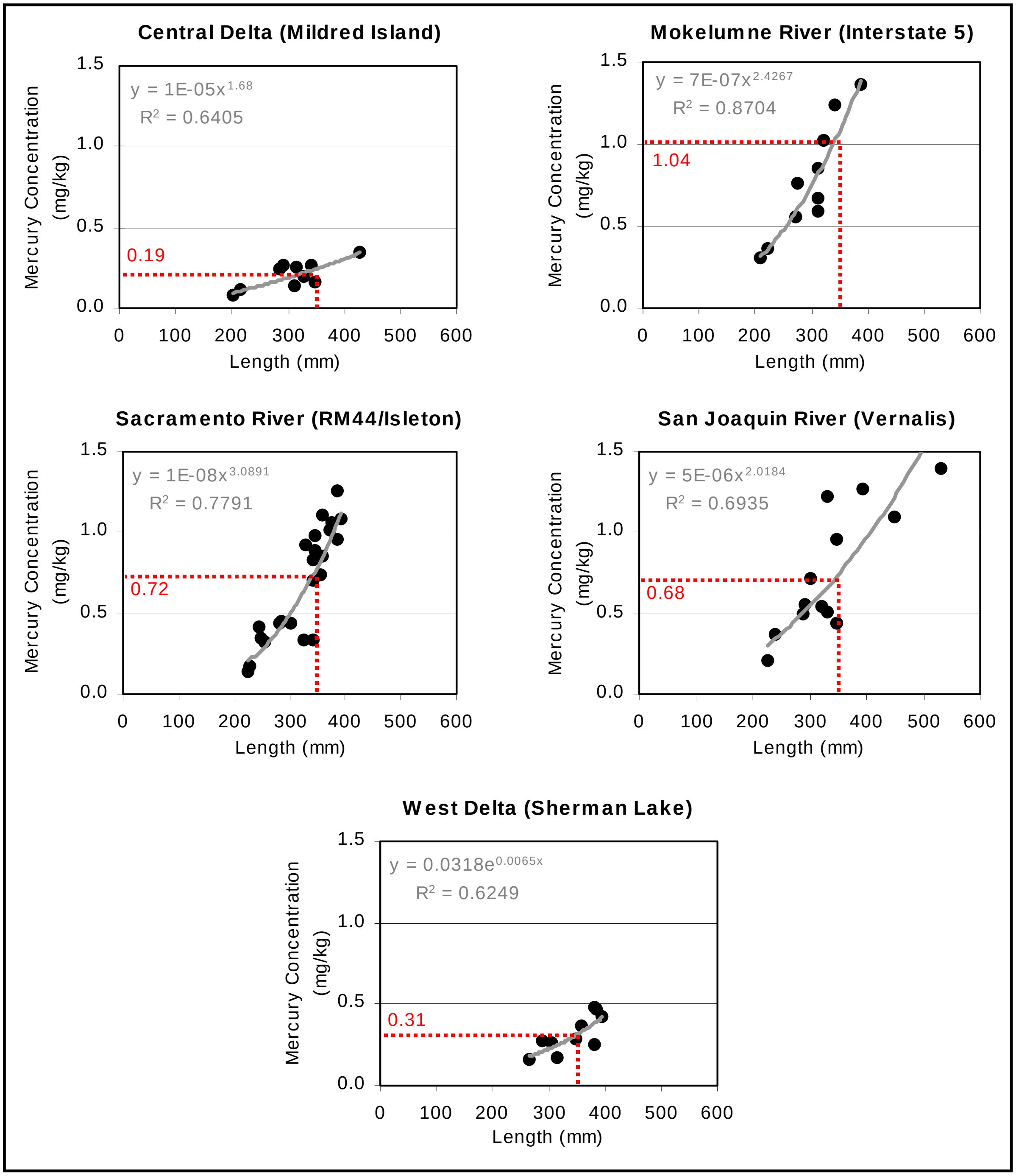

Figure 4.3: Site-specific Relationship between Largemouth Bass Length and Mercury Concentrations in the Delta. The relationships were used to predict the mercury content of a standard, 350-mm length bass sampled in September/October 2000, as indicated by the dashed lines. All relationships were significant at least at $P<0.05$.

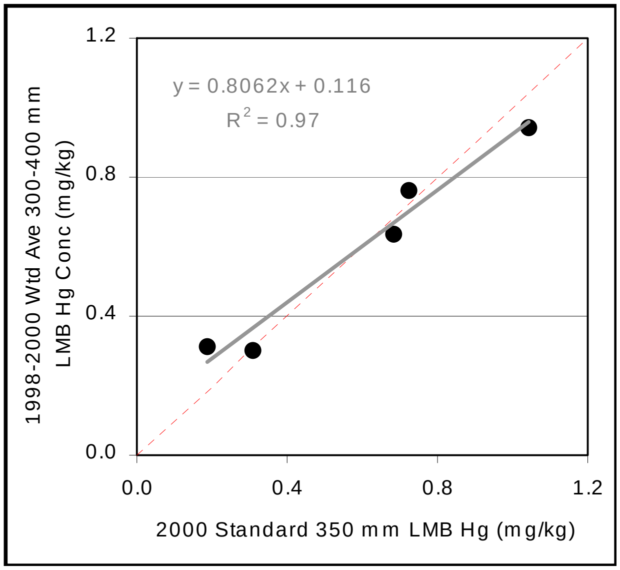

Figure 4.4: Comparison of Mercury Levels in Standard 350 mm Largemouth Bass (LMB) Collected at Linkage Sites in 2000 and Mercury Levels in 300-400 mm LMB Collected throughout Each Subarea in 1998-2000.

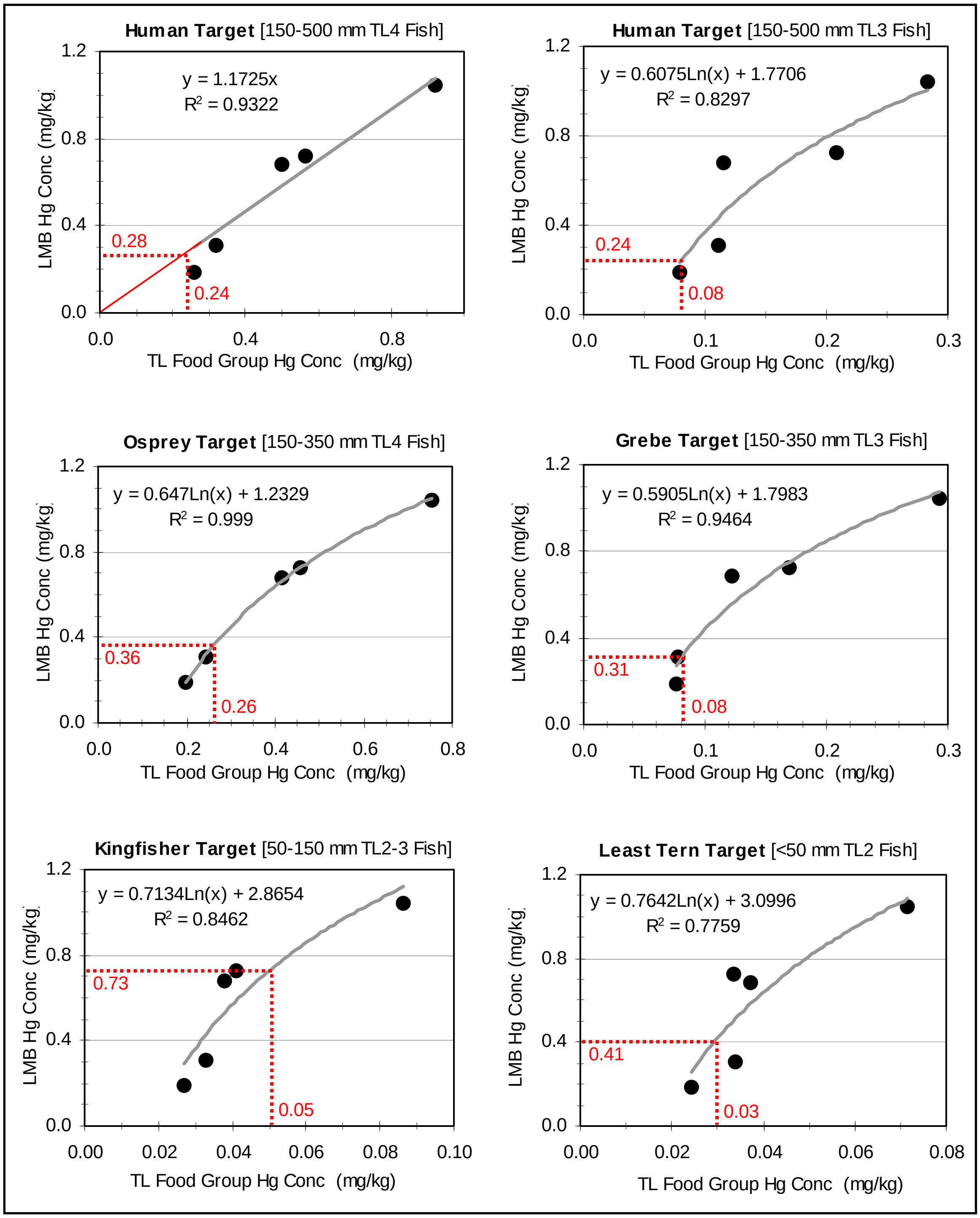

Figure 4.5: Comparison of Mercury Concentrations in Standard 350-mm Largemouth Bass (LMB) Caught in September/October 2000 and Composites of Fish from Various Trophic Level (TL) Food Groups Caught between 1998 and 2001.
The regressions are used to predict safe diets for target species listed in Table 4.9 in terms of largemouth bass mercury concentrations. Note, the recommended target for large TL4 fish (0.24 mg/kg) developed for human protection is lower than average mercury levels observed in the Delta, resulting in a corresponding standard 350-mm largemouth bass concentration that falls slightly below the regression curve based on observed values.

Key Points

- The concentration of methylmercury in fish tissue is the numeric target selected for the Delta methylmercury TMDL. Measurements of mercury in fish should be able to assess whether beneficial uses are being met because fish-eating (piscivorous) birds and mammals are most likely at risk for mercury toxicity.
- Piscivorous species identified in the Delta are: American mink, river otter, bald eagle, kingfisher, osprey, western grebe, common merganser, peregrine falcon, double crested cormorant, California least tern, and western snowy plover. Bald eagles, California least terns and peregrine falcons are listed by the State of California or by USFWS as either threatened or endangered species.
- Acceptable fish tissue levels of mercury for the trophic level food groups consumed by each wildlife species were calculated using the method developed by USFWS that addresses daily intake levels, body weights and consumption rates. Numeric targets were developed to protect humans in a manner analogous to targets for wildlife using USEPA-approved methods and regional information.
- Central Valley Water Board staff recommends two numeric targets for large fish: 0.24 mg/kg (wet weight) in muscle tissue of large trophic level four (TL4) fish such as bass and catfish and 0.08 mg/kg (wet weight) in muscle tissue of large TL3 fish such as carp and salmon. These targets are protective of (a) humans eating 32 g/day (1 meal/week) of commonly consumed, large fish; and (b) all wildlife species that consume large fish. The evaluation of the relationships between methylmercury concentrations in large TL4 fish and the other trophic level food groups indicated that wildlife species that consume smaller or lower trophic level fish would be protected by the large TL3 and TL4 fish targets developed for human protection.
- To ensure that wildlife species dining only on small fish are protected, staff proposes an additional target of 0.03 mg/kg methylmercury in whole TL2 and 3 fish less than 50 mm in length. This target represents the safe mercury level for prey consumed by the California least tern, a piscivorous species listed by the federal government as endangered. Such a target for small fish also would protect the Western snowy plover and other species that consume small fish.
- Elevated fish mercury concentrations occur along the periphery of the Delta while lower body burdens are measured in the central Delta. Percent reductions in fish methylmercury levels ranging from 0% to 74% will be needed to meet the numeric targets for wildlife and human health protection in all subareas of the Delta.
- The relationships between methylmercury concentrations in largemouth bass and the trophic level food groups also were examined because largemouth bass are a good bioindicator species and only largemouth bass data are available for the same sampling period and locations as the methylmercury water data available for the linkage analysis (next chapter). It was possible to describe safe mercury ingestion rates for wildlife species and humans in terms of the mercury concentration in a standard 350-mm largemouth bass. A methylmercury concentration of 0.24 mg/kg in 350-mm length largemouth bass would fully protect humans and piscivorous wildlife species and is proposed as an implementation goal for use in the linkage analysis and determination of methylmercury allocations for point and nonpoint sources.

Options to Consider

- A variety of assumptions can be made to calculate safe fish mercury levels for humans. For example, staff recommended targets of 0.08 mg/kg and 0.24 mg/kg for large TL3 and TL4 fish, respectively, because such targets are protective of a higher consumption rate (~1 meal per week) than that used to develop the USEPA criterion (~1 meal per 2 weeks) and because available information indicates that anglers take home a mixture of TL3 and TL4 species. Application of the USEPA criterion to large TL4 fish results in a target of 0.29 mg/kg. Use of the USEPA default consumption rates of fish from TL2 (21.7%), TL3 (45.7%) and TL4 (32.6%) produces a much higher target of 0.58 mg/kg for large TL4 fish. However, as the evaluations of trophic level food group and standard 350-mm largemouth bass mercury levels indicate, a target of 0.58 mg/kg for large TL4 fish would not protect several piscivorous wildlife species, such as bald eagle, osprey, river otter, grebe, merganser, and least tern. Large TL4 fish targets of 0.29, 0.24, or 0.05 mg/kg would be protective of these species. However, a large TL4 fish target of 0.05 mg/kg may not be attainable because it is well below regional background fish mercury levels observed in the western United States.

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5 LINKAGE ANALYSIS

The Delta linkage analysis focuses on the comparison of methylmercury concentrations in water and biota. As discussed in Chapter 2, methylmercury is the form of mercury that bioaccumulates in the food web. The relationship has not previously been evaluated in the Delta, but statistically significant, positive correlations have been reported between aqueous methylmercury and aquatic biota elsewhere (Brumbaugh *et al.*, 2001; Foe *et al.*, 2002; Slotton *et al.*, 2003; Tetra Tech, Inc., 2005a; Sveinsdottir and Mason, 2005), indicating that methylmercury concentrations in water are one of the primary factors determining methylmercury concentrations in fish. This linkage analysis develops a Delta-specific mathematical relationship between aqueous and biotic methylmercury concentrations. The relationship is used to determine an aqueous methylmercury goal that, if met, is predicted to produce safe fish tissue levels for both human and wildlife consumption (Chapter 4). The aqueous methylmercury goal is then used to allocate methylmercury reductions for within-Delta and tributary sources (Chapter 8).

The linkage analysis has three sections. The first section describes the available fish and aqueous methylmercury data. The second section illustrates the mathematical relationship between unfiltered water and largemouth bass methylmercury levels. The mathematical relationship is used to develop an unfiltered aqueous methylmercury goal of 0.06 ng/l that corresponds to the recommended fish tissue targets that are protective of humans and wildlife that consume Delta fish. The final section provides an alternate linkage using 0.45 μ filtered methylmercury water data. Results of these correlation-based linkages are comparable to results of more empirical linkage methods, such as the evaluation of Delta areas that currently achieve the implementation goal for largemouth bass, and the use of bioaccumulation factors to calculate an aqueous methylmercury goal.

5.1 Data Used in Linkage Analysis

<u>Fish</u>. Water and fish have not been sampled in the Delta for the specific purpose of developing a linkage analysis. As a result, there is an acceptable overlap for only a portion of the available fish and water data. This linkage analysis focuses on recently collected largemouth bass data for several reasons. First, largemouth bass was the only species systematically collected near many of the aqueous methylmercury sampling locations used to develop the methylmercury mass balance for the Delta (next section). Second, largemouth bass are piscivorous and have some of the highest mercury levels of any fish species evaluated in the Delta. Third, bass are abundant and widely distributed throughout the Delta. Fourth, bass have high site fidelity. That is, largemouth bass maintain a localized home range; most stay within a mile of a given waterway (Davis *et al.*, 2003). Such high site fidelity makes them useful bioindicators of spatial variation in mercury accumulation in the aquatic food chain. Finally, spatial trends across the Delta in standard 350-mm largemouth bass mercury levels are representative of spatial trends in the trophic level food group mercury levels (Section 4.7). Largemouth bass were collected from 19 locations in the Delta in August/September 1998, 26 locations in September/October 1999, and 22 locations in September/October 2000 (Davis *et al.*, 2000; Davis *et al*., 2003; LWA, 2003). The year 2000 largemouth bass data were used in the linkage analysis because the exposure period of these fish had the greatest overlap with the available water data. Monthly water data were collected during the last eight months of the life of the fish. Figure 5.1 shows the water and largemouth bass methylmercury sampling locations used in the linkage analysis. The mercury concentrations in standard 350-mm largemouth bass and the corresponding water data for each sampling location are presented in Table 5.1. Section 4.8 in Chapter 4 describes the method used to calculate standard 350-mm largemouth bass mercury concentrations.

Water. Unfiltered methylmercury water samples were collected periodically between March 2000 and April 2004 at multiple Delta locations (Figure 5.1, Tables D.1 and D.3 in Appendix D). The monthly March-October 2000[28] subset of this data has the greatest overlap with the lifespan of the largemouth bass sampled in September/October 2000. The March-October 2000 and March 2000 to April 2004 data were pooled by Delta subarea to calculate monthly averages (Tables D.2 and D.3).[29] These values were used to estimate average and median methylmercury concentrations for the March-October 2000 period and annual and seasonal average and median concentrations for the March 2000 to April 2004 period (Table 5.1).[30]

Table 5.1: Fish and Water Methylmercury Values by Delta Subarea.

	Delta Subarea [(a)]				
	Sacramento River	Mokelumne River	Central Delta	San Joaquin River	West Delta
FISH [Sampled in September/October 2000] (mg/kg)					
Standardized 350-mm Largemouth Bass	0.72	1.04	0.19	0.68	0.31
WATER [Sampled between March and October 2000] (ng/l)					
Average	0.120	0.140	0.055	0.147	0.087
Median	0.086	0.142	0.032	0.144	0.053
WATER [Sampled between March 2000 and April 2004] (ng/l)					
Annual Average	0.108	0.166	0.060	0.160	0.083
Annual Median	0.101	0.161	0.051	0.165	0.061
Cool Season Average [(b)]	0.137	0.221	0.087	0.172	0.106
Cool Season Median	0.138	0.246	0.077	0.175	0.095
Warm Season Average	0.094	0.146	0.050	0.156	0.075
Warm Season Median	0.089	0.146	0.040	0.162	0.055

(a) See Figure 5.1 for the location of each water and fish collection site.
(b) For this analysis, "cool season" is defined as November through February and "warm season" is defined as March through October.

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28 Coincidentally, March through October defines the season with warmer water temperatures. Aquatic biota may be more metabolically active and have a higher methylmercury bioaccumulation rate in summer. In addition, sulfate-reducing bacteria may have higher methylmercury production rates making this a critical bioaccumulation period.

29 The methylmercury concentrations for two periods – (a) March-October 2000 and (b) September 2000 to April 2004 – were compared at each sampling location in Figure 5.1 with a paired t-test to determine whether the mean concentrations for the two time periods were different. The tests indicated no significant difference ($P \leq 0.05$) for any location. Therefore, the data for March 2000 to April 2004 (a substantially larger database than that for March-October 2000) were also evaluated in the linkage analysis.

30 Monthly averages were used to ensure that the seasonal and annual values were not biased by months with different sample sizes.

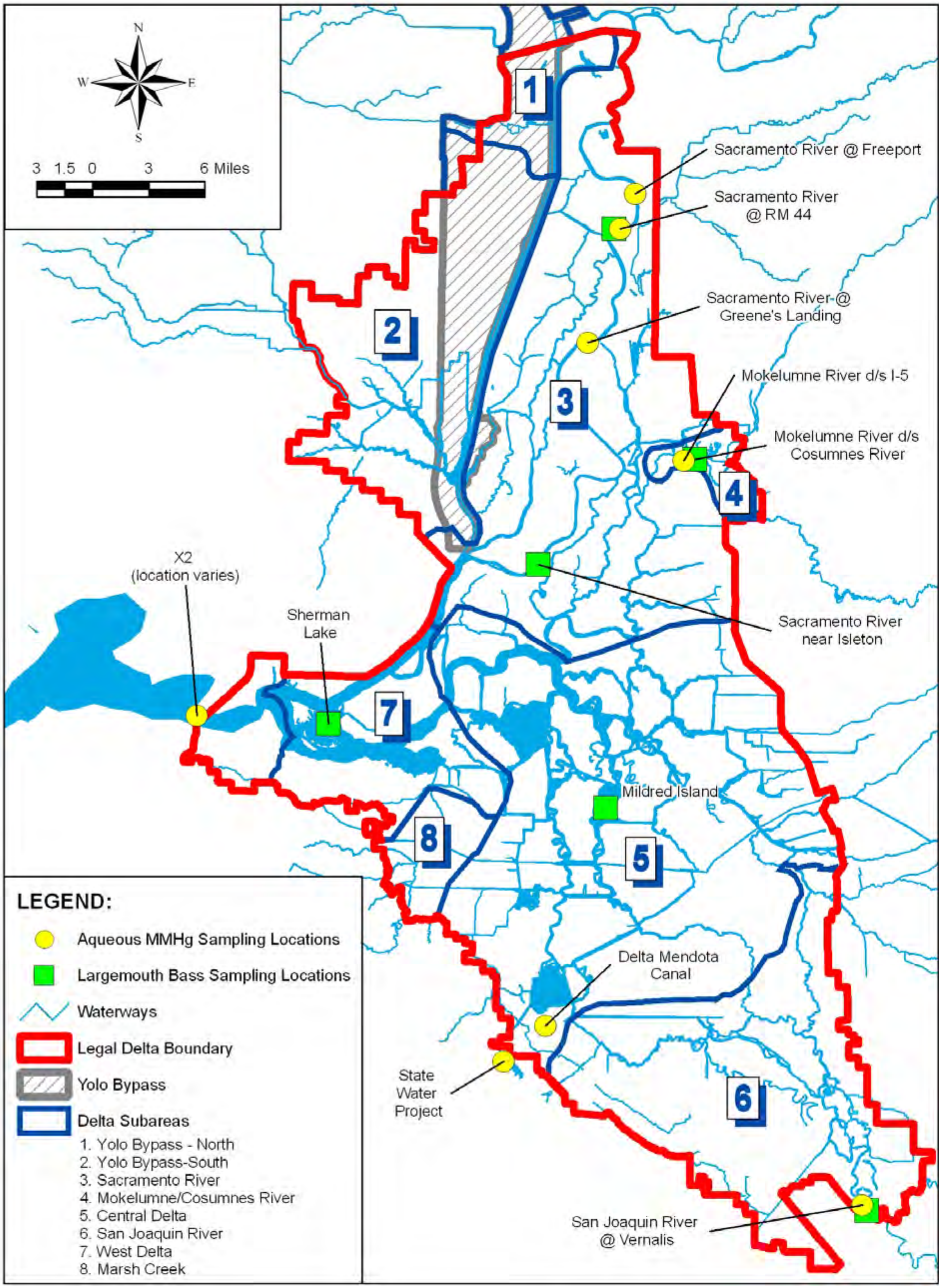

Figure 5.1: Aqueous and Largemouth Bass Methylmercury Sampling Locations Used in the Linkage Analysis.

5.2 Bass/Water Methylmercury Regressions & Calculation of Aqueous Methylmercury Goal

The mercury concentrations in standard 350-mm largemouth bass for each Delta subarea were regressed against the average and median unfiltered aqueous methylmercury levels for the March to October 2000 and March 2000 to April 2004 periods to determine whether relationships might exist (Figure 5.2, Table 5.2, and Figure D.1 in Appendix D). The regressions were evaluated using linear, exponential, logarithmic, and power curves. Power curves provided the best fit, although all the regression types demonstrated a positive relationship between aqueous and biotic methylmercury concentrations. In each scenario described by Table 5.2, increasing the aqueous methylmercury concentration results in increasing fish tissue levels. All the scenarios were statistically significant ($P < 0.05$). The recommended implementation goal for fish methylmercury in the Delta is 0.24 mg/kg (wet weight) in a standard 350-mm largemouth bass (Chapter 4). Substitution of 0.24 mg/kg into the equations in Table 5.2 results in predicted average and median safe water methylmercury values that range from 0.04 to 0.09 ng/l. The lowest concentration is predicted by the regression based on median March to October 2000 water values (Scenario 1B) while the highest concentration is predicted by the regression based on average cool season water concentrations (Scenario 3A).

Staff recommends that **0.06 ng/l methylmercury in unfiltered water** be used as an **implementation goal** for the determination of load allocations (Chapter 8). This recommendation is based on Scenario 1A in Table 5.2 and incorporates an explicit margin of safety of about 10%. The goal could be applied as an annual average methylmercury concentration. Staff recommends this value because only the March to October 2000 period overlapped the lifespan of the largemouth bass analyzed for mercury body burden. Also, little is known about the seasonal exposure regime controlling methylmercury concentrations in aquatic biota. Therefore, an annual average was selected as it weights all seasons equally.

The recommended implementation goals for largemouth bass and ambient water methylmercury in the Delta are based on Scenario B.4 from Table 4.5 in Chapter 4. Scenarios A.1, A.4, B.4 and E.3 are evaluated as fish tissue objective alternatives in the draft Basin Plan Amendment staff report. Table 5.3 shows the ambient water methylmercury levels that correspond to all the objective alternatives.

Progress towards attaining Alternative 5 in Table 5.3 would be difficult to track. This is because Alternative 5 (0.05 mg/kg in large TL4 fish) is substantially below existing conditions anywhere in the Delta, thus making it difficult to accurately extrapolate from methylmercury in fish to corresponding methylmercury in water. Such extrapolation for Alternative 5 produces a concentration of 0.028 ng/l methylmercury in water, which is below the current minimum reporting level for laboratory analyses for methylmercury. (Minimum reporting levels are equivalent to the lowest calibration standard for methylmercury, which is currently 0.05 ng/l.) Though water methylmercury concentrations below the minimum reporting level can be detected, they cannot be quantified accurately; thus, Alternative 5 progress would be difficult to quantify and track. The other fish tissue objective alternatives correspond to water methylmercury concentrations above the minimum reporting level of 0.05 ng/l and thus can be quantified accurately.

The linkage analysis for the Delta relies upon sequential correlations to determine the numerical aqueous methylmercury goal. A potential problem with the analysis is that each correlation has an associated error term. No attempt has been made to estimate these errors and propagate them from one correlation to the next when calculating the recommended aqueous methylmercury goal.

There are two alternate, more empirical, approaches. The first approach is to compare existing largemouth bass and aqueous methylmercury levels to the proposed implementation goals. The average March-October 2000 methylmercury concentration in the Central Delta (0.055 ng/l, Table 5.1) is less than the proposed aqueous goal of 0.06 ng/l while concentrations in the West Delta (0.087 ng/l) are higher. Similarly, the methylmercury concentration in standard 350-mm bass in the Central Delta is 0.19 mg/kg while the concentration in the West Delta is 0.31 mg/kg (Table 4.10). The recommended implementation goal is 0.24 mg/kg in standard 350-mm largemouth bass. Therefore, empirical observations suggest that the "correct" aqueous methylmercury goal to achieve safe mercury levels in the various trophic level food groups must lie between 0.055 and 0.087 ng/l. If the aqueous methylmercury goal of 0.06 ng/l is attained in the Delta, then methylmercury concentrations in all trophic level food groups are predicted to fall within the safe tissue concentration range.

A second linkage approach that does not rely on the correlation between largemouth bass and water methylmercury concentrations to derive an implementation goal for water makes use of bioaccumulation factors (BAFs), an approach used in numerous USEPA-approved TMDLs across the country.[31] A BAF is the ratio of the concentration of a chemical in fish tissue to the concentration of the chemical in the water column. As defined in the Mercury Study Report to Congress (USEPA, 1997a), the BAF is the concentration of the methylmercury in fish divided by the concentration of dissolved methylmercury in water. A total BAF based on the total concentration of a chemical in water also can be used (USEPA, 2003). By definition, BAFs imply a linear relationship between methylmercury in the water column and in fish. Section D.2 in Appendix D describes the method used to develop BAF-based implementation goals for the Delta and its subareas using standard 350-mm largemouth bass and average aqueous methylmercury concentrations. The resulting safe aqueous methylmercury levels ranged from 0.029 to 0.069 ng/l, and averaged 0.052 ng/l:

- Central Delta subarea: 0.069 ng/l;
- Mokelumne River subarea: 0.032 ng/l;
- Sacramento River subarea: 0.040 ng/l;
- San Joaquin River subarea: 0.052 ng/l; and
- West Delta subarea: 0.067 ng/l.

These levels are slightly less than but comparable to the safe levels produced using the regression-based approach. The similarity most likely occurs because both methods used the same fish and water data, and because the regression described in Figure 5.2(A) is nearly linear at low fish and water methylmercury levels. This approach has the benefit that it does not assume identical bioaccumulation rates across the Delta. However, unlike the regression-

[31] Refer to: http://www.epa.gov/OWOW/tmdl/index.html.

based method, the BAFs inherently assume a linear relationship between fish and water methylmercury levels.

The safe aqueous methylmercury concentrations predicted for the Delta are comparable to analysis results for Cache Creek and nationwide studies. Brumbaugh and others (2001) found in a national survey of 106 stations from 21 basins that one-time unfiltered methylmercury water samples collected during the fall season were also positively correlated with largemouth bass tissue levels. An aqueous methylmercury concentration of 0.058 ng/l was predicted to produce three-year old largemouth bass[32] with 0.3 mg/kg mercury tissue concentration. In the Cache Creek watershed, an unfiltered methylmercury concentration of 0.14 ng/l corresponded with the production of 0.23 mg/kg mercury in large fish (Cooke *et al.*, 2004). Predicted safe methylmercury water values for the Delta are bracketed by safe water concentrations determined by the national and Cache Creek studies.

Additional fish and methylmercury water studies that address uncertainties in the linkage analysis are planned. These include additional evaluations of standard 350-mm largemouth bass tissue concentrations at more locations in the Delta and elsewhere in the Central Valley after multiple years of aqueous methylmercury data have been obtained. Studies also are planned to better determine the seasonal exposure regime when most of the methylmercury is sequestered in the aquatic food chain. Board staff will work with a statistician to develop a more powerful statistical analysis of the linkage during the study period. The results of these studies may lead to future revisions in the proposed aqueous methylmercury goal.

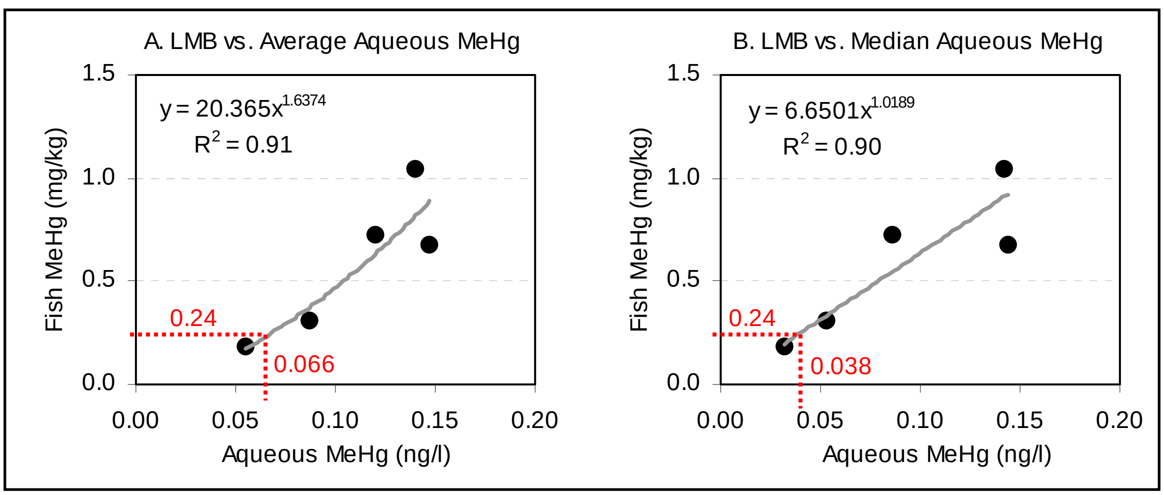

Figure 5.2: Relationships between Standard 350-mm Largemouth Bass Methylmercury and March to October 2000 Unfiltered Aqueous Methylmercury.
The proposed implementation goal for standard 350-mm largemouth bass is 0.24 mg/kg.

[32] 262-mm average length fish.

Table 5.2: Relationships between Methylmercury Concentrations in Water and Standard 350-mm Largemouth Bass

Aqueous MeHg Data Period	Scenario	Regression Equation	$R^{2 (a)}$	Aqueous MeHg Conc. (ng/l) Corresponding to LMB value of 0.24 mg/kg
1. March to October 2000	A. Average Aqueous MeHg	$y = 20.365x^{1.6374}$	0.91	0.066
	B. Median Aqueous MeHg	$y = 6.6501x^{1.0189}$	0.90	0.038
2. March 2000 to April 2004 - Annual -	A. Average Aqueous MeHg	$y = 14.381x^{1.51}$	0.88	0.066
	B. Median Aqueous MeHg	$y = 8.0903x^{1.1926}$	0.86	0.052
3. March 2000 to April 2004 - Cool Season -	A. Average Aqueous MeHg	$y = 17.795x^{1.8007}$	0.90	0.092
	B. Median Aqueous MeHg	$y = 8.8725x^{1.4347}$	0.92	0.081
4. March 2000 to April 2004 - Warm Season -	A. Average Aqueous MeHg	$y = 11.528x^{1.339}$	0.83	0.055
	B. Median Aqueous MeHg	$y = 6.8941x^{1.0723}$	0.85	0.044

(a) All R^2 values are statistically significant at P<0.05. Regression graphs are provided in Figure 5.2 and Appendix D.

Table 5.3. Ambient Water Methylmercury Concentrations that Correspond to Alternative Fish Tissue Objectives Evaluated in the Basin Plan Amendment Staff Report.

Fish Tissue Objective Alternative [(a)]	**Scenario # from Table 4.5**	**150-500 mm TL3 Fish Tissue Target** (mg/kg)	**150-500 mm TL4 Fish Tissue Target** (mg/kg)	**Predicted Standard 350-mm Largemouth Bass (LMB) MeHg Concentration for TL3 Fish Target** (mg/kg) [(b)]	**Predicted Standard 350-mm LMB MeHg Concentration for TL3 Fish Target** (mg/kg) [(b)]	**Ambient Water MeHg Concentration that Corresponds to the Lowest Predicted LMB Concentration for the Alternative** (ng/l) [(b)]
2	A.1	0.20	0.58	0.79	0.68	0.125
3	A.5	- - -	0.29		0.34	0.082
4	B.4	0.08	0.24	0.24	0.28	0.066
5	E.3	- - -	0.05		0.06	0.028

(a) Alternative numbers from Table 3.1 in the Basin Plan Amendment Staff Report. "Alternative 1" is the "no action" alternative and has a narrative objective rather than a numeric objective.

(b) Predicted standard 350-mm largemouth bass methylmercury concentrations that correspond to the TL3 fish targets were calculated using the equation provided in Figure 4.5 for "Human Target [150-500 TL3 Fish]". Predicted standard 350-mm largemouth bass methylmercury concentrations that correspond to the TL4 fish targets are based on the equation provided in Figure 4.5 for "Human Target [150-500 TL4 Fish]".

(c) Ambient water methylmercury concentrations that correspond to the predicted largemouth bass concentrations were calculated using the equation for Scenario 1A in Table 5.2.

5.3 Evaluation of a Filtered Aqueous Methylmercury Linkage Analysis

This section presents an alternate linkage analysis based on filter-passing[33] aqueous methylmercury data. Methylmercury concentrations in standard 350-mm largemouth bass for each Delta subarea (Table 5.1) were regressed against the average and median filtered aqueous methylmercury levels for March-October 2000 (Table 5.4 and Table D.4 in Appendix D). Figure 5.3 demonstrates that there is a statistically significant positive correlation between filter-passing aqueous and largemouth bass tissue methylmercury levels. However,

[33] Water samples were filtered using 0.45-micrometer capsule filters. Much of the methylmercury measured in filtered samples is colloidal (Choe, 2002). Hence the results are called "filter-passing" rather than "dissolved".

average and median filter-passing methylmercury water values for the Central Delta and Western Delta, regions that define the lower end of the regression, are determined mainly by values lower than the method detection limit (0.022 ng/l). Furthermore, substitution of the recommended implementation goal of 0.24 mg/kg mercury for 350 mm largemouth bass in the equations in Figure 5.3 results in predicted average and median safe water values (0.016 ng/l and 0.010 ng/l, respectively) below the method detection limit. Similarly low levels resulted when the BAF-based linkage method was used (see Section D.2 in Appendix D). Staff does not recommend adoption of a methylmercury goal that is unquantifiable with present analytical methods.

Key points to consider for the linkage analysis are listed after Table 5.4 and Figure 5.3.

Table 5.4: Average and Median Filtered Methylmercury Concentrations (ng/l) for March 2000 to October 2000 for Each Delta Subarea.

	Delta Subarea [(a)]				
	Sacramento River	Mokelumne River	Central Delta	San Joaquin River	West Delta
Average	0.043	0.078	0.029	0.037	0.019
Median	0.039	0.069	0.014	0.036	0.011

(a) See Figure 5.1 for the location of each water and fish collection site. See Appendix L for raw data and Table D.4 in Appendix D for monthly averages, upon which these average and median values are based.

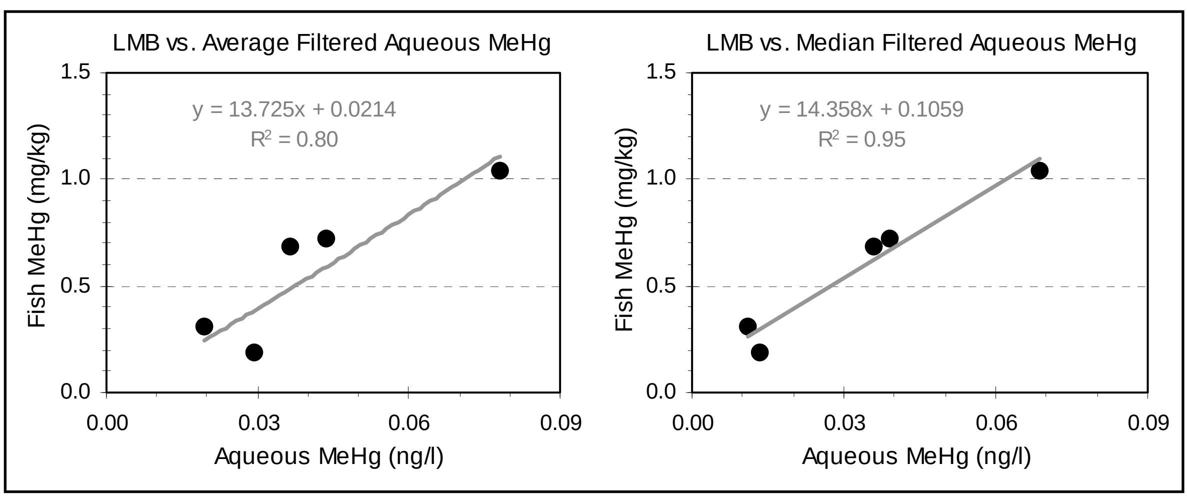

Figure 5.3: Relationships between Standard 350-mm Largemouth Bass Mercury Levels and March to October 2000 Filtered Aqueous Methylmercury.

Key Points

- Statistically significant mathematical relationships exist between unfiltered and filter-passing methylmercury concentrations in water and fish tissue.
- Based on the relationship between average March to October 2000 unfiltered methylmercury concentrations in water and methylmercury in standard 350-mm largemouth bass tissue, staff recommends an implementation goal for ambient Delta waters of 0.06 ng/l unfiltered methylmercury. The proposed goal incorporates an explicit margin of safety of about 10%. Staff recommends that the goal be applied as an annual average methylmercury concentration.
- More empirical linkage methods, such as the evaluation of Delta areas that currently achieve the implementation goal for largemouth bass and the use of bioaccumulation factors to calculate an aqueous methylmercury goal, predict safe aqueous methylmercury levels comparable to the correlation-based linkage method.

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