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# Spatial trends and impairment assessment of mercury in sport fish in the Sacramento–San Joaquin Delta watershed

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*Regional differences in sport fish mercury were found in the Sacramento–San Joaquin Delta.*

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ABSTRACT

A three-year study was conducted to examine mercury in sport fish from the Sacramento–San Joaquin Delta. More than 4000 fish from 31 species were collected and analyzed for total mercury in individual muscle filets. Largemouth bass and striped bass were the most contaminated, averaging 0.40 μg/g, while redear sunfish, bluegill and rainbow trout exhibited the lowest (<0.15 μg/g) concentrations. Spatial variation in mercury was evaluated with an analysis of covariance model, which accounted for variability due to fish size and regional hydrology. Significant regional differences in mercury were apparent in size-standardized largemouth bass, with concentrations on the Cosumnes and Mokelumne rivers significantly higher than the central and western Delta. Significant prey–predator mercury correlations were also apparent, which may explain a significant proportion of the spatial variation in the watershed.



## 1. Introduction

Mercury, a heavy metal that is highly toxic in the organic form methylmercury, is known to accumulate to concentrations of concern in food webs of the Sacramento–San Joaquin Delta (henceforth "Delta") and its watershed (Davis et al., 2008a). The mercury problem in California dates back to the 19th century when mercury was mined from the Coast Range and transported to the Sierra Nevada for use in gold extraction. Historical releases of mercury from gold mining areas were substantial (1.4–3.6 million kg; USGS, 2000), and in many watersheds mercury continues to wash downstream from these areas today.

Methylmercury can pose a problem when it bioaccumulates through the food web at concentrations of concern for humans or wildlife. The primary route of exposure for humans is through the consumption of contaminated fish. Studies conducted during 1998–2000 in the Delta, found mercury at concentrations of concern for human health in striped bass, largemouth bass, white catfish, and other popular sport fish species (Davis et al., 2000, 2008a; Wood et al., 2006). This is of particular concern because almost all mercury in fish is in the form of methylmercury, which has a high affinity for proteins in edible fish muscle (Bloom, 1992). Methylmercury is one of the most toxic forms of mercury, which has been linked with irreversible damage to the developing human central nervous system (Choi, 1990; Mergler et al., 2007). In the Delta, one of the most popular areas for sport and subsistence fishing in California, exposure to methylmercury is of particular concern for human health and water quality managers (Silver et al., 2007). In the past few years, numerous consumption advisories have been issued by the California Office of Environmental Health Hazard Assessment (OEHHA) for the Delta and its watershed (e.g., Gassel et al., 2006; Klasing et al., 2006), which is a clear indication of the concern for human health exposure to methylmercury in sport fish from this region.

The Fish Mercury Project ('FMP' or 'Project') was a three-year study to examine mercury in sport fish from the Delta watershed and to increase public awareness of fish contamination issues. The overall goal of the Project was to help reduce short-term methylmercury exposure to humans and wildlife. The Project closely followed recommendations of the California Bay Delta Authority (CBDA) "Mercury Strategy" (Wiener et al., 2003) to monitor fish in support of adaptive management of the mercury problem. The

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most frequently sampled sport fish species were largemouth bass, redear sunfish, bluegill, common carp, Sacramento sucker, rainbow trout, white catfish, channel catfish, striped bass, and Sacramento pikeminnow. The other major components of the FMP were an equally significant effort investigating mercury in biosentinel fish (short lived, small fish) species and a largemouth bass food web model. This paper integrates all of these aspects of the study to address the two main objectives:

1) To characterize mercury concentrations in sport fish to assess the health risks of consuming contaminated fish, and
2) To characterize spatial and inter-annual trends in mercury in the piscine food web.

## 2. Methods

### 2.1. Sampling and design

Fish sampling focused on species commonly caught by sport and subsistence fishers. Primary targets were dependent on the region of the watershed being sampled, with largemouth bass, Sacramento sucker, common carp, redear sunfish, and bluegill being the most frequently caught species in this study. Largemouth bass were sampled at a wide range of total lengths to model regional and site-specific differences in length:mercury relationships (Tremblay et al., 1995, 1998). Secondary target species were collected when primary targets were unavailable, with channel catfish, Sacramento pikeminnow, rainbow trout, and white catfish being the most common. A detailed analysis of striped bass data will be presented separately in a companion article in conjunction with the Regional Monitoring Program for Water Quality in the San Francisco Estuary, but the data for striped bass have been included here when relevant. Sample sizes for the main target species (largemouth bass) often met our sampling objective of 12 individuals per site. For other species, the target of five individuals was met at many sites, depending on the species' geographic range. In total, 31 species, representing more than 4000 individual fish, were collected.

Sport fish were collected from locations in the Sacramento–San Joaquin Delta watershed during May 2005 through December 2007 (Fig. 1, Table 1). One hundred and twenty-four FMP sampling locations were designated for sampling; these included popular fishing areas and provided broad geographic coverage across the watershed. In addition to the FMP sites, the Sacramento River Watershed Program sampled fish at three sites in 2005, and the Central Valley Regional Water Quality Control Board also collected fish from 19 sites in 2005 and 2006. Collaboration with these agencies allowed for a greater geographic scope in sampling, and coordination ensured no duplication of effort. Data from all 146 sites are included in this paper. Fish were collected using clean-hands technique by Moss Landing Marine Laboratories staff with an electrofisher boat and fyke nets. The secondary target species caught during this time were also kept. Total length (longest length from tip of tail fin to tip of nose/mouth), fork length (longest length from tail fork to tip of nose/mouth), and weight (for larger fish) were measured in the field. Information on bycatch, including species and approximate numbers of non-target species, was recorded. Fish were wrapped in chemically cleaned Teflon sheeting and frozen on dry ice for transportation to the laboratory.

### 2.2. Analytical and QA/QC

Fish were kept frozen wrapped in Teflon in their original bags until the time of dissection. Dissection of individual muscle tissue samples was performed following US EPA guidance (US EPA, 2000). At the time of dissection, fish were placed in a clean lab in their original bags to thaw. After thawing, fish were cleaned by rinsing with de-ionized (DI) and ASTM Type II water, and were handled only by personnel wearing polyethylene or powder-free latex gloves (glove type is analyte dependent). All dissection materials were cleaned by scrubbing with Micro® detergent, rinsing with tap water, DI water, and finally ASTM Type II water. All fish were dissected skin-off, and only the fillet muscle tissue was used for analysis.

Total mercury in muscle tissue was measured at Moss Landing Marine Laboratories. The lab analyzed all fish as individuals. Tissue samples were analyzed according to EPA 7473, "Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry" with a Milestone Direct Mercury Analyzer (Model DMA-80). Clean techniques were followed during preparation of samples, blanks, and standards, using ASTM Type II water and analytical grade chemicals. A continuing calibration verification (CCV) was performed after every 10 samples, and samples run between CCVs that drifted greater than 10% were rerun. Three blanks, a standard reference material (DORM-2), a duplicate sample, and a pair of spiked samples were analyzed with each set of samples.

The mercury samples were analyzed in multiple batches. Batches consisted of 20 samples per batch. Standard Reference Material (NRC-DORM-2: dogfish muscle) recoveries were within the acceptable range of 75%–125% recovery (range for all species 88%–112%) established by the CalFed QAPP (Puckett and van Buuren, 2000). The mercury matrix spike recoveries were all within the acceptable range of 75%–125% recovery (range for all species 76%–125%). Relative Percent Differences (RPDs) for spiked samples were within the acceptable range of less than 25% (range for all species 0%–17%). All of the mercury lab duplicate RPDs were also in the acceptable range below 25% (range for all species 0%–10%), and all method blanks were below the detection limit. Mercury concentrations were reported in μg/g or parts-per-million, wet weight.

Moss Landing Marine Labs participated in an inter-comparison study implemented for all California Bay Delta Authority mercury projects (van Buuren, 2006) in 2005 and 2006. Three percent (3%) of MLMLs tissue samples (40 samples) were sent to an independent laboratory (Frontier GeoSciences in Washington State) in each year to assess the reliability of results. Analysis shows that the RPDs between labs for the field samples were within the acceptable range of 0%–25%.

### 2.3. Data analysis

#### 2.3.1. Concentration categories

Mercury concentrations are presented in four categories loosely based on Advisory Tissue Levels by the California Office of Environmental Health Hazard Assessment (OEHHA) (Klasing and Brodberg, 2008). The lowest concentration category used in this paper (less than 0.1 μg/g) is a range where OEHHA generally encourages consumption. The highest concentrations (above 0.4 μg/g) are in a range where OEHHA generally discourages consumption for women of childbearing age and for children 17 and younger. Intermediate categories were developed to bridge the gap between these endpoints, thus 0.1–0.25 μg/g and 0.25–0.4 μg/g were used.

#### 2.3.2. Controlling for length:mercury relationships

Two methods were used to control for the relationship of fish length to mercury concentration within species. A general linear modeling approach (analysis of covariance) was used when data were sufficient (see below). Size limits (Table 2, Supplemental Table 1) were applied, when comparing regions, for all other species. US EPA guidance (US EPA, 2000) specifies that the smallest fish in a composite should be no less than 75% the length of the largest. This guidance was used to control for length of individual fish in the study by establishing size limit categories in each species.

#### 2.3.3. Predicting spatial and temporal differences in mercury concentrations

A general linear mixed model (PROC MIXED in SAS v. 9.1; Littell et al., 1996) was used to examine spatial variation in mercury concentrations and the length:mercury relationship in largemouth bass. In the description given below, the model procedure and model effects are capitalized for emphasis. PROC MIXED estimates model parameters (i.e., slope and intercept) with numerical maximum likelihood techniques and allows for the rigorous modeling of random effects. This approach has two main advantages. First, the maximum likelihood model selection procedure allows non-nested models to be compared to each other. Second, treating sampling site as a random effect (see below) provides a basis for drawing inferences regarding similar habitats throughout the study area. Thus, the findings can be more confidently extrapolated to the full region rather than just to the particular sampling locations.

To analyze large-scale differences in mercury, spatial variation was examined by treating REGION as a fixed effect in the model, which represented the major river or water source for the area. Ten different regions were identified in the Project sample space, which encompassed the major rivers and tributaries of the Sacramento–San Joaquin Delta watershed (see below on data included). SITE was treated as a random effect (nested within REGION) under the assumption that the sampled sites were representative of the universe of possible sites within the study area. Fish length (LENGTH) and a squared length term ($LENGTH^2$) were included as covariates to evaluate support for linear and quadratic relationships between LENGTH and MERCURY in the model. Finally, we included first-order interaction terms between both length terms and SITE and REGION to model spatial variation in length:mercury relationships. The full model containing all effects can be expressed as:

$$
\begin{aligned}
MERCURY_{(ijk)} = {} & \beta_0 + \left(\beta_{REGION} \times REGION_{(i)} + \varepsilon_{SITE_{(j)}\left(REGION_{(i)}\right)}\right) + \beta_{LENGTH} \times LENGTH_{(k)} \\
& + \beta_{LENGTH} \times LENGTH^2_{(k)} + \beta_{REGION_{(i)} \times LENGTH}\left(REGION_{(i)} \times LENGTH_{(k)}\right) \\
& + \varepsilon_{SITE_{(j)}\left(REGION_{(i)}\right) \times LENGTH}\left(SITE_{(j)} \times LENGTH_{(k)}\right) \\
& + \beta_{REGION_{(i)} \times LENGTH^2}\left(REGION_{(i)} \times LENGTH^2_{(k)}\right) \\
& + \varepsilon_{SITE_{(j)}\left(REGION_{(i)}\right) \times LENGTH^2}\left(SITE_{(j)} \times LENGTH^2_{(k)}\right) + \varepsilon_{ijk}
\end{aligned}
$$

where $MERCURY_{(ijk)}$ is the mercury concentration (μg/g, wet wt) for fish $k$ caught at site $j$ of region $i$, $\beta_0$ is the model intercept, $\beta_{REGION(i)}$ is the effect of region $i$ on mercury concentration, $REGION_{(i)}$ is the dummy variable associated with region $i$, $\beta_{LENGTH}$ is the slope term for fish length, $LENGTH_{(k)}$ was the length (mm) of fish $k$, $\beta_{LENGTH^2}$ is the slope term for the square of fish length, $LENGTH^2_{(k)}$ was squared length of fish $k$, $\varepsilon_{SITE(j)\ (REGION(i))}$ is the random error in mercury concentration associated with site $j$ nested within region $i$, $\varepsilon_{SITE(j)\ (REGION(i)) \times LENGTH}$ is the random error associated with the interaction between site $j$ and fish length, $\varepsilon_{SITE(j)\ (REGION(i)) \times LENGTH^2}$ is the random

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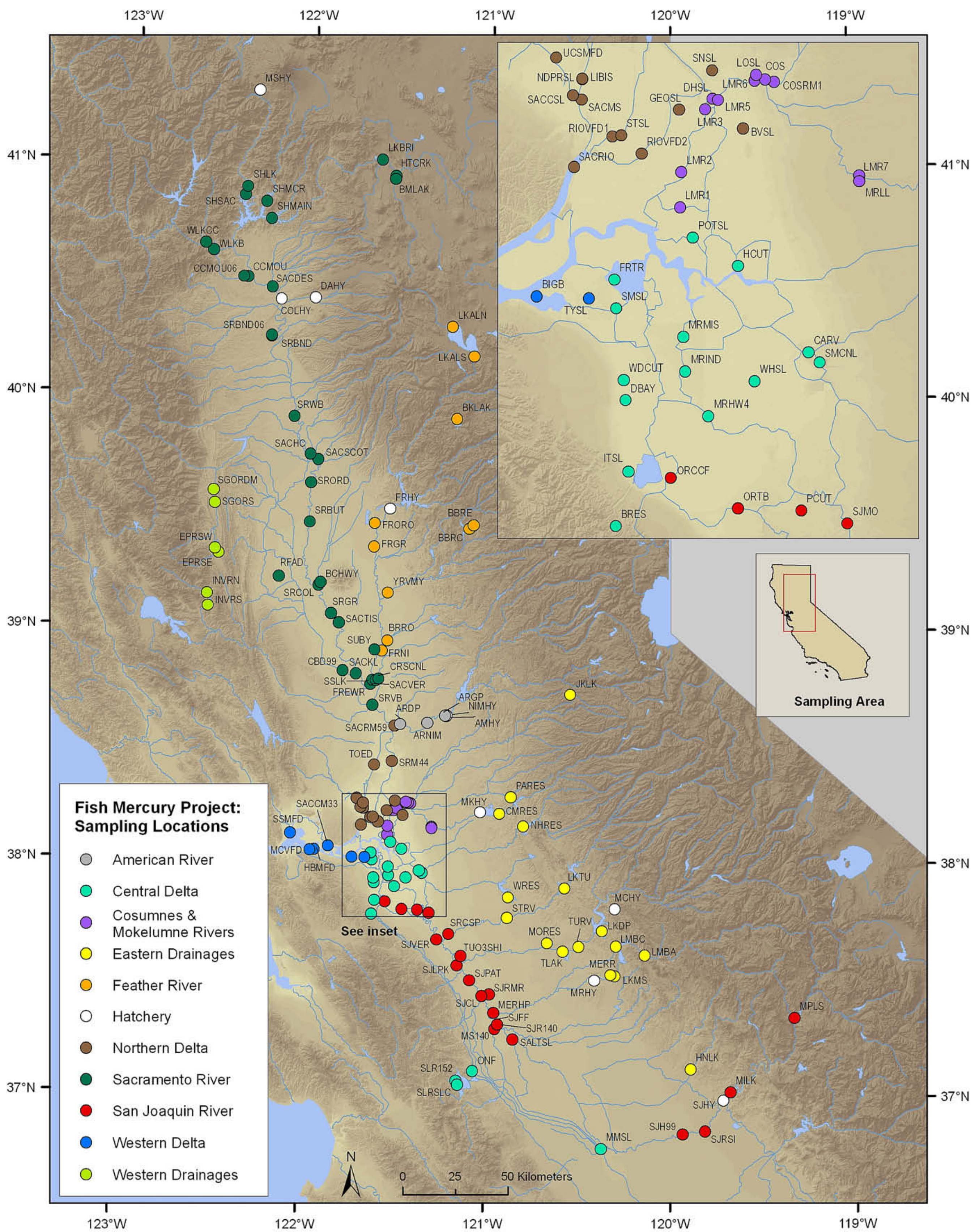


**Fig. 1.** Sport fish sampling locations (2005–2007). See Table 1 for site names corresponding to site codes.

**Table 1**
Fish Mercury Project sampling locations 2005–2007.

| Station code | Station name | Year(s) sampled | Region | Waterbody type |
|---|---|---|---|---|
| AMHY | American Hatchery | 2005 | Hatchery | Hatchery |
| ARDP | American River at Discovery Park | 2005 | American River | River |
| ARGP | American River at Goethe Park | 2005 | American River | River |
| ARNIM | American River at Hazel Ave and Nimbus Dam | 2005, 2006 | American River | River |
| BBRC | Bullards Bar Reservoir at Central | 2006 | Feather River | Lake/Reservoir |
| BBRE | Bullards Bar Reservoir at East Arm | 2006 | Feather River | Lake/Reservoir |
| BCHWY | Butte Creek at Colusa Highway | 2006 | Sacramento River | River |
| BIGB | Big Break | 2005, 2007 | Western Delta | River |
| BKLAK | Bucks Lake | 2006 | Feather River | Lake/Reservoir |
| BMLAK | Baum Lake | 2006 | Sacramento River | Lake/Reservoir |
| BRES | Bethany Reservoir | 2007 | San Joaquin River | Lake/Reservoir |
| BRRO | Bear River at Rio Oso | 2005 | Feather River | River |
| BVSL | Beaver Slough | 2005 | Northern Delta | River |
| CARV | Calaveras River | 2005 | Central Delta | River |
| CBD99 | Colusa Basin Drain at Road 99E | 2005 | Sacramento River | River |
| CCMOU | Clear Creek | 2005 | Sacramento River | River |
| CCMOU06 | Clear Creek Near Mouth | 2006 | Sacramento River | River |
| CMRES | Camanche Reservoir | 2005 | Eastern Drainages | Lake/Reservoir |
| COLHY | Coleman Hatchery | 2005 | Hatchery | Hatchery |
| COS | Cosumnes River | 2005, 2007 | Cos/Mok Rivers | River |
| COSRM1 | Cosumnes River at River Mile 1 | 2006 | Cos/Mok Rivers | River |
| CRSCNL | Cross Canal | 2006 | Sacramento River | River |
| DAHY | Darrah Springs Hatchery | 2005 | Hatchery | Hatchery |
| DBAY | Discovery Bay | 2005 | Central Delta | River |
| DHSL | Dead Horse Slough | 2007 | Cos/Mok Rivers | River |
| EPRSE | East Park Reservoir Southeast | 2006 | Western Drainages | Lake/Reservoir |
| EPRSW | East Park Reservoir West | 2006 | Western Drainages | Lake/Reservoir |
| FREWR | Fremont Weir | 2006 | Sacramento River | River |
| FRGR | Feather River at Gridley | 2005, 2006 | Feather River | River |
| FRHY | Feather River Hatchery | 2005 | Hatchery | Hatchery |
| FRNI | Feather River at Nicolaus | 2005 | Feather River | River |
| FRORO | Feather River at Oroville Outlet | 2006 | Feather River | River |
| FRTR | Frank's Tract | 2005, 2007 | Central Delta | River |
| GEOSL | Georgiana Slough | 2006 | Northern Delta | River |
| HBMFD | Honker Bay (McAvoy Fish Derby) | 2006 | Western Delta | River |
| HCUT | Honker Cut | 2005 | Central Delta | River |
| HNLK | Hensly Lake | 2007 | San Joaquin River | Lake/Reservoir |
| HTCRK | Hat Creek | 2006 | Sacramento River | River |
| INVRN | Indian Valley Reservoir North | 2006 | Western Drainages | Lake/Reservoir |
| INVRS | Indian Valley Reservoir South | 2006 | Western Drainages | Lake/Reservoir |
| ITSL | Italian Slough | 2005 | Central Delta | River |
| JKLK | Jenkinson Lake | 2005 | Eastern Drainages | Lake/Reservoir |
| LIBIS | Liberty Island | 2006 | Northern Delta | River |
| LKALN | Lake Almanor North | 2006 | Feather River | Lake/Reservoir |
| LKALS | Lake Almanor South | 2006 | Feather River | Lake/Reservoir |
| LKBRI | Lake Britton | 2006 | Sacramento River | Lake/Reservoir |
| LKDP | Lake Don Pedro | 2007 | San Joaquin River | Lake/Reservoir |
| LKMS | Lake McSwain | 2007 | San Joaquin River | Lake/Reservoir |
| LKTU | Lake Tulloch | 2007 | San Joaquin River | Lake/Reservoir |
| LMBA | Lake McClure at Bagby | 2007 | San Joaquin River | Lake/Reservoir |
| LMBC | Lake McClure at Barrett Cos | 2007 | San Joaquin River | Lake/Reservoir |
| LMR1 | Lower Mokelumne River 1 | 2007 | Cos/Mok Rivers | River |
| LMR2 | Lower Mokelumne River 2 | 2007 | Cos/Mok Rivers | River |
| LMR3 | Lower Mokelumne River 3 | 2007 | Cos/Mok Rivers | River |
| LMR5 | Lower Mokelumne River 5 | 2007 | Cos/Mok Rivers | River |
| LMR6 | Lower Mokelumne River 6 | 2007 | Cos/Mok Rivers | River |
| LMR7 | Lower Mokelumne River 7 | 2007 | Cos/Mok Rivers | River |
| LOSL | Lost Slough | 2005 | Cos/Mok Rivers | River |
| MCHY | Moccasin Hatchery | 2005 | Hatchery | Hatchery |
| MCVFD | Ryer Island (McAvoy Fish Derby) | 2006 | Western Delta | River |
| MERHP | Merced River at Hatfield State Park | 2005, 2006 | San Joaquin River | River |
| MERR | Merced River | 2007 | San Joaquin River | River |
| MILK | Millerton Lake | 2005 | Eastern Drainages | Lake/Reservoir |
| MKHY | Mokelumne Hatchery | 2005 | Hatchery | Hatchery |
| MMSL | Mendota Pool/Mendota Slough | 2005, 2007 | Central Delta | River |
| MORES | Modesto Reservoir | 2007 | San Joaquin River | Lake/Reservoir |
| MPLS | Mammoth Pools | 2007 | Eastern Drainages | Lake/Reservoir |
| MRHW4 | Middle River at HWY 4 | 2005 | Central Delta | River |
| MRHY | Merced Hatchery | 2005 | Hatchery | Hatchery |
| MRIND | Middle River at Bullfrog | 2005, 2007 | Central Delta | River |
| MRLL | Mokelumne River at Lodi Lake | 2005 | Cos/Mok Rivers | River |
| MRMIS | Middle River at Mildred Island | 2005 | Central Delta | River |
| MS140 | Mud Slough at HWY 140 | 2007 | San Joaquin River | River |
| MSHY | Mount Shasta Hatchery | 2005 | Hatchery | Hatchery |
| NDPRSL | Prospect Slough | 2005, 2007 | Northern Delta | River |

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**Table 1** (*continued* )

| Station code | Station name | Year(s) sampled | Region | Waterbody type |
|---|---|---|---|---|
| NHRES | New Hogan Reservoir | 2005 | Eastern Drainages | Lake/Reservoir |
| NIMHY | Nimbus Hatchery | 2005 | Hatchery | Hatchery |
| ONF | O'Neal Forebay | 2007 | San Joaquin River | Lake/Reservoir |
| ORCCF | Old River at Cliffton Court Forebay | 2006 | San Joaquin River | River |
| ORTB | Old River at Tracy Blvd. | 2005 | San Joaquin River | River |
| PARES | Pardee Reservoir | 2005 | Eastern Drainages | Lake/Reservoir |
| PCUT | Paradise Cut | 2005 | San Joaquin River | River |
| POTSL | Potato Slough | 2005, 2007 | Central Delta | River |
| RFAD | Rice fields/Agricultural Ditches | 2006 | Sacramento River | Other |
| RIOVFD1 | Rio Vista Fish Derby1 | 2006 | Northern Delta | River |
| RIOVFD2 | Rio Vista Fish Derby2 | 2006 | Northern Delta | River |
| SACCM33 | Sacramento River at Channel Marker 33 | 2006 | Western Delta | River |
| SACCSL | Sacramento River at Cache Slough | 2006 | Northern Delta | River |
| SACDES | Sacramento River Near Deschutes Rd | 2006 | Sacramento River | River |
| SACHC | Sacramento River at Hamilton City | 2005 | Sacramento River | River |
| SACKL | Sacramento River at Knights Landing | 2006 | Sacramento River | River |
| SACMS | Sacramento River at Miner Slough | 2006 | Northern Delta | River |
| SACRIO | Sacramento River at Rio Vista | 2005, 2007 | Northern Delta | River |
| SACRM59 | Sacramento River – West Sacramento at River Mile 59 – Between Discovery Park and Miller Park | 2006 | Northern Delta | River |
| SACSCOT | Sacramento River Near Hamilton (Scotty's Boat Landing) | 2006 | Sacramento River | River |
| SACTIS | Sacramento River at Tisdale Boat Ramp AKA River Bend Marina | 2006 | Sacramento River | River |
| SACVER | Sacramento River Near Verona Marina, Village Resort AKA Joe's Place | 2006 | Sacramento River | River |
| SALTSL | Salt Slough at Hwy 165 | 2005 | Central Delta | River |
| SGORDM | Stony Gorge Reservoir at Dam | 2006 | Western Drainages | Lake/Reservoir |
| SGORS | Stony Gorge Reservoir South | 2006 | Western Drainages | Lake/Reservoir |
| SHLK | Shasta Lake | 2006 | Sacramento River | Lake/Reservoir |
| SHMAIN | Shasta Lake Main Stem | 2006 | Sacramento River | Lake/Reservoir |
| SHMCR | Shasta Lake at McCloud River | 2006 | Sacramento River | Lake/Reservoir |
| SHSAC | Shasta Lake at Sacramento River | 2006 | Sacramento River | Lake/Reservoir |
| SJCL | San Joaquin River at Crows Landing | 2005 | San Joaquin River | River |
| SJFF | San Joaquin River at Fremont Ford | 2005 | San Joaquin River | River |
| SJH99 | San Joaquin River at HWY 99 | 2005 | San Joaquin River | River |
| SJHY | San Joaquin Hatchery | 2005 | Hatchery | Hatchery |
| SJLPK | San Joaquin River at Laird Park | 2005 | San Joaquin River | River |
| SJMO | San Joaquin River at Mossdale | 2005 | San Joaquin River | River |
| SJPAT | San Joaquin River at Patterson | 2005 | San Joaquin River | River |
| SJR140 | San Joaquin River at HWY 140 | 2007 | San Joaquin River | River |
| SJRMR | San Joaquin River at Merced River | 2007 | San Joaquin River | River |
| SJRSI | San Joaquin River at Sycamore Island | 2007 | San Joaquin River | River |
| SJVER | San Joaquin River at Vernalis | 2005, 2007 | San Joaquin River | River |
| SLR152 | San Luis Reservoir at HWY 152 | 2007 | San Joaquin River | Lake/Reservoir |
| SLRSLC | San Luis Reservoir at San Luis Creek | 2007 | San Joaquin River | Lake/Reservoir |
| SMCNL | Smith Canal | 2005 | Central Delta | River |
| SMSL | Sand Mound Slough | 2005 | Central Delta | River |
| SNSL | Snodgrass Slough Near Delta Meadows | 2006 | Northern Delta | River |
| SRBND | Sacramento River at Bend Bridge | 2005 | Sacramento River | River |
| SRBND06 | Sacramento River at Bend Bridge Near Red Bluff | 2006 | Sacramento River | River |
| SRBUT | Sacramento River at Butte City | 2005 | Sacramento River | River |
| SRCOL | Sacramento River at Colusa | 2005, 2006 | Sacramento River | River |
| SRCSP | Stanislaus River at Caswell State Park | 2005 | San Joaquin River | River |
| SRGR | Sacramento River at Grimes | 2005 | Sacramento River | River |
| SRM44 | Sacramento River at RM44 | 2005, 2007 | Northern Delta | River |
| SRORD | Sacramento River at Ord Bend | 2005 | Sacramento River | River |
| SRVB | Sacramento River at Veterans Bridge | 2005 | Sacramento River | River |
| SRWB | Sacramento River at Woodson Bridge | 2005 | Sacramento River | River |
| SSLK | Sacramento Slough at Karnak | 2005 | Sacramento River | River |
| SSMFD | Suisun Slough (McAvoy Fish Derby) | 2006 | Western Delta | River |
| STRV | Stanislaus River | 2007 | San Joaquin River | River |
| STSL | Steamboat Slough | 2006 | Northern Delta | River |
| SUBY | Sutter Bypass Below Kirkville Road | 2006 | Sacramento River | River |
| TLAK | Turlock Lake | 2007 | San Joaquin River | Lake/Reservoir |
| TOED | Toe Drain | 2006, 2007 | Northern Delta | River |
| TUO3SHI | Tuolumne River at Shiloh Rd. | 2005 | San Joaquin River | River |
| TURV | Tuolumne River | 2007 | San Joaquin River | River |
| TYSL | Taylor Slough | 2005 | Western Delta | River |
| UCSMFD | Upper Cache Slough (McAvoy Fish Derby) | 2006 | Northern Delta | River |
| WDCUT | Werner Dredger Cut | 2005 | Central Delta | River |
| WHSL | Whiskey Slough | 2005 | Central Delta | River |
| WLKB | Whiskeytown Lake at Brandy Creek | 2006 | Sacramento River | Lake/Reservoir |
| WLKCC | Whiskeytown Lake at Clear Creek | 2006 | Sacramento River | Lake/Reservoir |
| WRES | Woodward Reservoir | 2007 | San Joaquin River | Lake/Reservoir |
| YRVMY | Yuba River at Marysville | 2005 | Feather River | River |

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**Table 2**
Fish species sampled ($n > 55$). Length limits were used to control for size in the comparison to concentration categories in Fig. 2.

| Common name | Genus | Species | Length limits (mm) | Number of samples within length limits |
|---|---|---|---|---|
| Largemouth bass | *Micropterus* | *salmoides* | 307–435 | 466 |
| Redear sunfish | *Lepomis* | *microlophus* | 152–228 | 234 |
| Bluegill | *Lepomis* | *macrochirus* | 116–176 | 220 |
| Common carp | *Cyprinus* | *carpio* | 434–659 | 201 |
| Sacramento sucker | *Catostomus* | *occidentalis* | 329–489 | 195 |
| Rainbow trout | *Oncorhynchus* | *mykiss* | 262–381 | 143 |
| White catfish | *Ameiurus* | *catus* | 243–378 | 124 |
| Channel catfish | *Ictalurus* | *punctatus* | 367–518 | 117 |
| Striped bass | *Morone* | *saxatilis* | 479–702 | 78 |
| Sacramento pikeminnow | *Ptychocheilus* | *grandis* | 257–472 | 77 |

error associated with the interaction between site $j$ and the square of fish length, and $\varepsilon_{ijk}$ is the random error associated fish $k$ caught at site $j$ of region $i$. The random errors are normally and independently distributed with a mean of zero.

A combined dataset of all three years of data was used in the linear model analysis of spatial effects. However, in general, different sites were sampled in different years. Thus, spatial and temporal effects were to a certain extent confounded. Our approach was to treat site as a random factor and acknowledge that any temporal variation was included in the random site term. Note that differences in mercury due to inter-annual variation were also modeled separately (see below). Only sites with at least nine samples and a 130 mm or greater range in lengths were included in the analysis.

An information-theoretic approach (Burnham and Anderson, 2002) was used to evaluate support for a suite of *a priori* models, where each model contained a different combination of the parameters described above. Specifically, Akaike's Information Criteria (AIC) corrected for small samples sizes ($AIC_c$) was used to rank each of the competing models based on the level of support from the data. $AIC_c$ is a statistic used to estimate the relative distance between competing models and the unknown true model that generated the data. Therefore, the model with the smallest $AIC_c$ value indicates the "closest" to unknown reality. Furthermore, in the calculation of $AIC_c$, models are penalized for the number of parameters. Thus, $AIC_c$ selects the model that fits the data best and also has the smallest number of parameters (i.e., simplicity and parsimony). In addition, $AIC_c$ weights were computed to determine the strength of evidence for each competing model to supplement inferences made simply from $AIC_c$ values. $AIC_c$ weights represent the probability that a model being evaluated is the "best" among the suite of candidate models. $AIC_c$ values and $AIC_c$ model weights were calculated using the formulas given in Burnham and Anderson (2002).

The modeling procedure first estimated the level of support for different combinations of random effects, using restricted maximum likelihood methods. All fixed effects were included in this stage of the model. Once the appropriate random effects structure was identified, the procedure evaluated the level of support for models with different combinations of fixed effects. The model with the greatest $AIC_c$ weight and lowest $AIC_c$ value was selected for the final model, but models within 1–2 $AIC_c$ values were considered to be competing models (Burnham and Anderson, 2002).

The next step was to test whether the relationship between fish length and mercury concentrations differed among regions. First, the method employed dummy variables to determine differences in means, slopes, and curve shapes among locations. The resulting regression equations were used to calculate predicted mercury concentrations (mean and 95% confidence interval) for each location at a standardized total length of 350 mm. The 350-mm standard size was selected based on the peak in the length-frequency distribution of largemouth bass sampled in the Project. Finally, the model tested for differences among regions using linear contrasts of mean mercury concentration. This procedure consisted of a least-squares means test with multiple comparison adjustment for the $p$-values and confidence limits. The analysis assessed the probability that the difference in estimated mean mercury concentrations between regions based on a 350-mm standardized length fish was significantly different from zero.

As mentioned previously, some level of inter-annual variation was included in our results of the spatial analysis. Therefore, to address this question, a dataset of eight sampling locations was used to examine temporal differences in mercury across the watershed (2005 vs. 2007). Additionally, five of those eight sites overlapped with the dataset from 2000 summarized in Davis et al. (2008a,b), and thus were also included in this analysis. As described for analysis of spatial effects, restricted maximum likelihood (REML) methods were used to estimate parameters and competing models were ranked with AICc model selection criteria. Using the selected model from PROC MIXED, the relationship between fish length and mercury concentrations was tested between years for each location at 350-mm standardized length. The same procedure using linear contrasts described above was used to examine variation among years.

### 2.4. Mapping and GIS methods

The map figures were designed with ESRI ArcInfo 9.1 software and are in a California Teale Albers NAD 83 Projection. A connection to the GIS from the SWAMP Tissue 2.5 database (Microsoft Access 2003) was established to display the locations and results of queries.

## 3. Results and Discussion

### 3.1. Variation in mercury among species

Mercury concentrations in all target species sampled within the applied length limits exceeded the 0.10 µg/g threshold in some samples (Table 2, Fig. 2, Supplemental Table 1). Striped bass and largemouth bass exhibited the highest proportion of samples with concentrations above 0.40 µg/g. Among all sites, striped bass averaged 0.40 µg/g with 50% of the samples exceeding 0.40 µg/g, and an additional 33% from 0.25 to 0.40 µg/g. Largemouth bass was the most intensively sampled species ($n = 466$), and also exhibited an average concentration of 0.40 µg/g. Forty percent (40%) of largemouth bass exceeded 0.40 µg/g and only four largemouth bass were below 0.10 µg/g. These results suggest that both striped bass and largemouth bass could be significant dietary sources of methylmercury to consumers of these species in the Delta (OEHHA, 1994; Gassel et al., 2006).

Sacramento pikeminnow was sampled the least frequently of the target species ($n = 77$), but was among the most contaminated. Twenty-three percent (23%) of the samples exceeded 0.40 µg/g, which ranked third highest after striped bass and largemouth bass. White catfish and channel catfish were relatively well sampled ($n > 100$), and indicated moderate mercury levels. In both species, the largest proportion of samples (51% and 43%, respectively) corresponded to 0.1–0.25 µg/g.

Common carp and Sacramento sucker are known to grow relatively large, and are omnivorous, primarily feeding on benthic-dwelling organisms (Moyle, 2002). The vast majority of common carp samples exceeded 0.10 µg/g, with approximately one-third in each of the 0.10–0.25 µg/g (34%) and 0.25–0.40 µg/g (37%) categories. Most of the remaining samples were even higher in concentration, with 21% exceeding 0.40 µg/g. In all likelihood, the relatively high concentrations and wide range in mercury found in common carp can be attributed to its large size (434–659 mm) and variable diet that changes with age (Becker, 1983; Moyle, 2002). Sacramento sucker, like largemouth bass and common carp, exhibited some higher concentrations, with most of the samples (42%) from 0.10 to 0.25 µg/g. However, likely due to a diet of primarily algae, detritus, and small benthic invertebrates (Moyle, 2002), few suckers (7%) exceeded 0.40 µg/g and more than one-quarter (28%) were below 0.10 µg/g.

Redear sunfish and bluegill were the smallest species sampled and were relatively low in mercury. These species averaged 0.12 µg/g

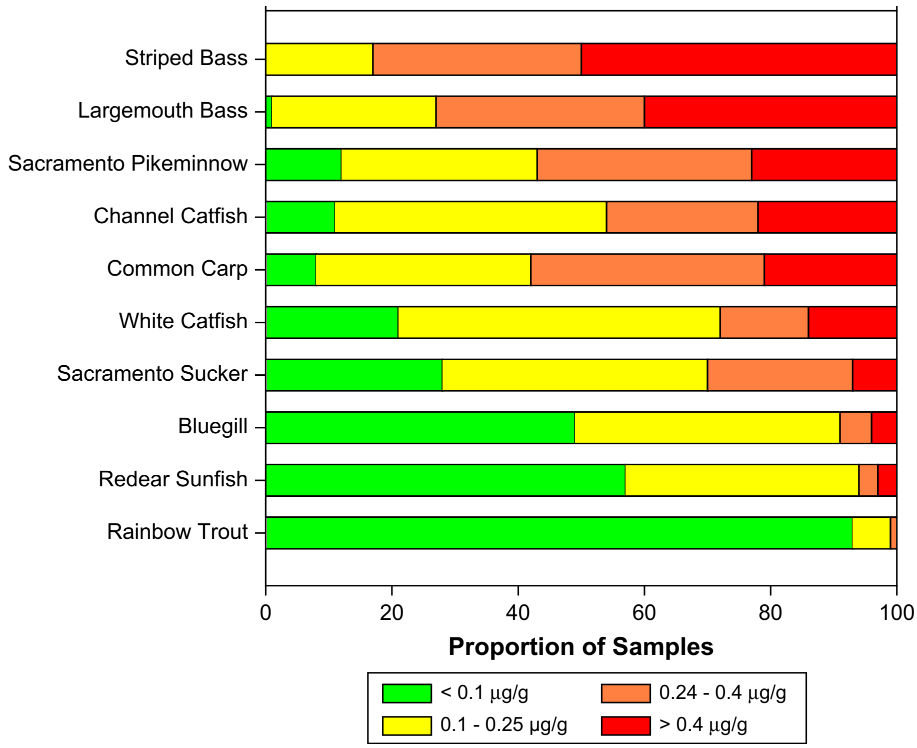


**Fig. 2.** Comparison to mercury concentration categories in primary species sampled ($n > 55$). Size was constrained using length limits in Table 2.

and 0.14 µg/g, respectively. Approximately half of the redear and bluegill samples (57% and 49%, respectively) were below 0.10 µg/g, suggesting that consumption of these species may contribute to low levels of dietary mercury exposure. Rainbow trout exhibited the lowest mercury concentrations of all the target species. Mercury concentrations averaged 0.04 µg/g across all sites. Nearly all samples (93%) corresponded to the <0.1 µg/g category, with the remaining 7% from 0.10 to 0.40 µg/g.

The relative degree of mercury contamination among species sampled in the Project was expected, based on their feeding ecology and trophic positions. Largemouth bass and striped bass are large sport fish (up to 579 mm and 1149 mm, respectively, in this study) and are top piscivores inhabiting the Delta watershed. Adults are known to consume all varieties of fish and large invertebrates that are found in their habitat (Moyle, 2002). A high exposure to methylmercury was therefore anticipated in these species, given their size and position in the food web. Common carp, Sacramento sucker, and channel catfish also grow rather large (commonly > 400 mm in this study), but their diets do not primarily consist of fish. Rather, detritus and benthic invertebrates are primary food items. Similarly, rainbow trout are insectivores, consuming surface-dwelling invertebrates (Moyle, 2002). These species were the least contaminated of the large fish sampled in the Project. Redear sunfish and bluegill are relatively small in size and occupy a lower position in the food web (Moyle, 2002), feeding primarily on shelled invertebrates (particularly clams and crustaceans). Therefore, the lower concentrations in bluegill, redear sunfish, and rainbow trout were predictable due to different diets compared to other species sampled in the Project.

The results of this study suggest that redear sunfish and bluegill are species lower in mercury, and thus may be good alternatives to species such as striped bass, largemouth bass, and other piscivores for limiting human dietary mercury exposure. Rainbow trout were consistently low in mercury as well, with the highest concentration found in the Project being 0.36 µg/g. However, the trout were generally distributed over a different spatial range than the other species sampled in the Project, as they were primarily found in high-elevation lakes.

### 3.2. Spatial differences in mercury concentrations

The second main purpose of sport fish sampling was to characterize spatial trends in mercury accumulation in the piscine food web. The model selection procedure indicated that the effects of total length, site, and region represented the ‘best’ model to examine spatial variation in largemouth bass mercury concentrations. A component of this model not implemented in previous analysis of covariance models of fish mercury concentrations in the Delta (e.g., Davis et al., 2008a), is the inclusion of a random spatial variable to represent the sampling site, which allows our results to be inferred across the full study area. The authors acknowledge that site selection was not strictly random, however, due to the wide geographic coverage of sites ($n = 146$ locations), we assume these data to be representative of the entire study area. With this approach, we can make inferences regarding locations not sampled from similar habitats within the study area. However, the patterns that can be assessed with the data in hand are spatial trends across all sites and regions, without reference to specific habitat types.

Since largemouth bass exhibited some of the highest concentrations in the Project, comparison of standardized length bass (350-mm fish) to the concentration categories (Fig. 3) provides a worst-case picture of the mercury problem across the watershed. Standardized mercury concentrations were above 0.10 µg/g at all sites evaluated, with the highest proportion of sites (29 of 67, 43%) corresponding to the >0.40 µg/g category. The Sacramento River, Feather River, eastern drainages, and north Delta exhibited relatively similar average concentrations that ranged from 0.33 to 0.48 µg/g (Fig. 4). The highest concentrations were found on the Cosumnes and Mokelumne Rivers, which averaged 0.83 ± 0.40 µg/g. The large confidence intervals in this region were due to one site (Mokelumne

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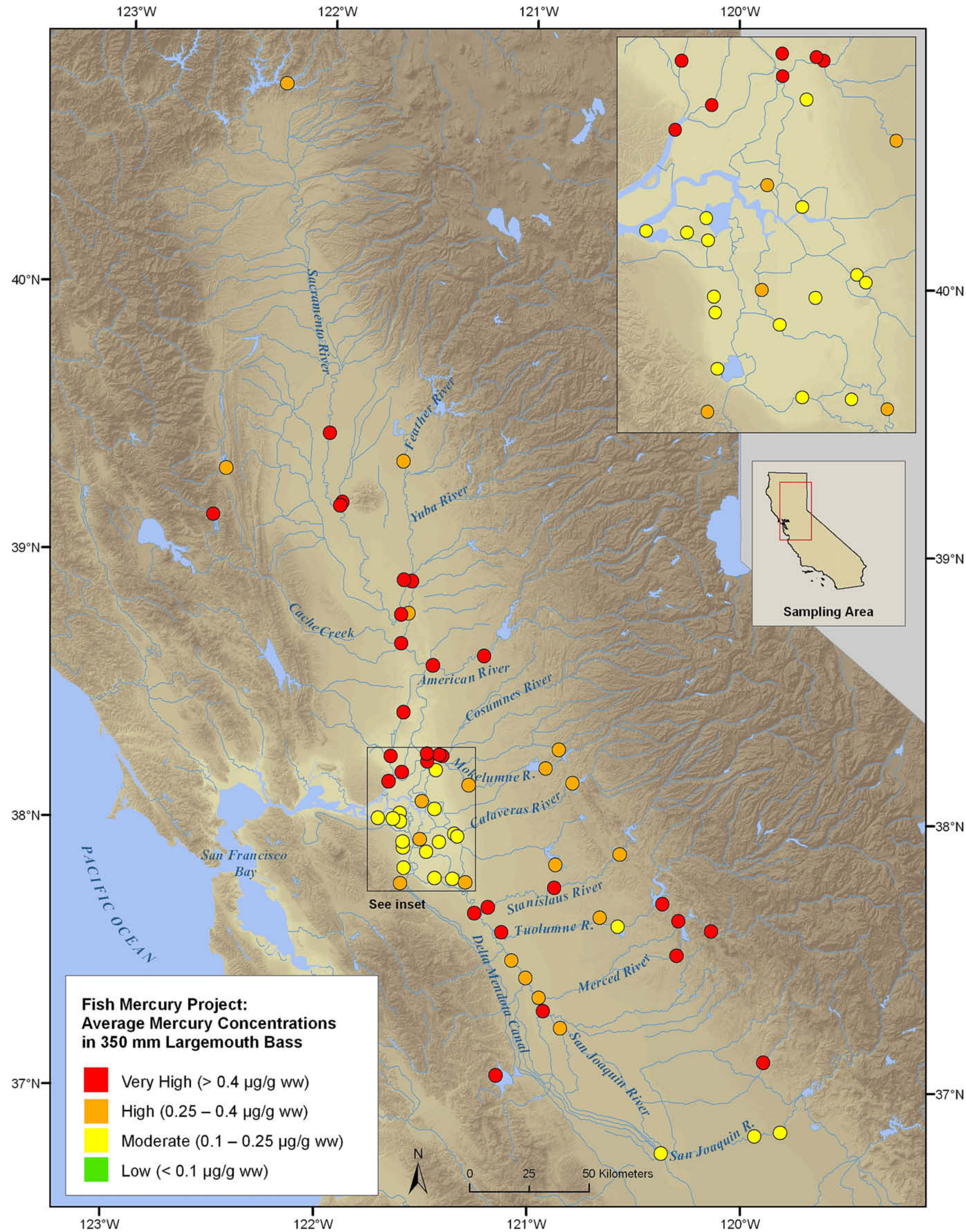


**Fig. 3.** Mercury concentrations in 350-mm largemouth bass. No sites corresponded to <0.1 µg/g.

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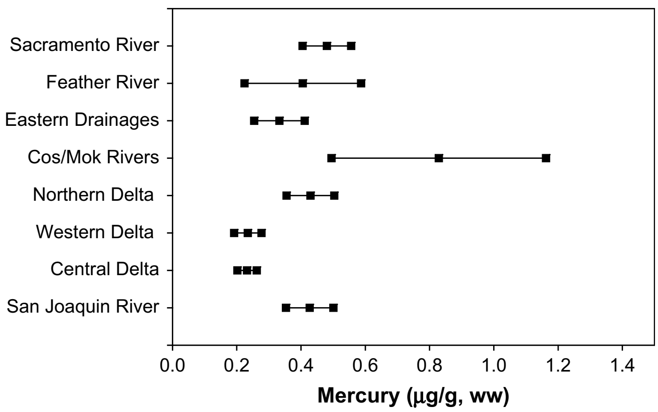


**Fig. 4.** Predicted mercury concentrations (mean ± 95% confidence intervals) for 350-mm largemouth bass in each region. Regions represented by three or more sites were included. Refer to Table 1 for list of sites included in each of the region categories.

River at Lodi Lake) where concentrations in fish were much lower than at the other sites. In contrast, moderate (0.10–0.25 µg/g) mercury concentrations were evident in the central Delta (0.23 µg/g) and lower San Joaquin River region (0.43 µg/g). A few sites in the southern portion of the San Joaquin watershed had concentrations above 0.40 µg/g. However, most of these were not located on the major rivers, but in lakes and reservoirs at higher elevation. Unfortunately, statistical evaluation of mercury by habitat type was not feasible with these data. However, a statewide sampling of largemouth bass from lakes and reservoirs is currently being conducted by the Surface Water Ambient Monitoring Program (Davis et al., 2008b). Site-specific estimates for 350-mm largemouth bass are presented in Supplemental Table 2. Statistical comparison of means indicated that locations along the Cosumnes and Mokelumne Rivers had significantly higher concentrations ($p < 0.001$) than locations in all other regions of the watershed. The central Delta was significantly lower than the Sacramento River ($t = -3.29$, $p = 0.001$) and the San Joaquin River ($t = -3.38$, $p = 0.008$). This spatial pattern corroborates the most recent study in the region (Davis et al., 2008a), but with nearly three times as many locations included in the analysis.

For all other species not analyzed by the modeling approach, length and sample size limits were applied to compare average mercury concentrations among the different regions of the watershed. Striped bass and common carp, the two largest fish species, followed the same general pattern in mercury as largemouth bass (Table 3). Striped bass were sampled at three sites in each of the Sacramento River, north Delta, and San Joaquin River regions. Each region averaged over 0.40 µg/g, with bass on the San Joaquin River having the highest concentrations (0.52 ± 0.20 µg/g). Mercury concentrations are often highly variable in striped bass due to their relatively large size, variable diet, and large movement patterns of individuals (Moyle, 2002). Common carp were lower in mercury than the two bass species. Average mercury concentrations in carp were greater than 0.25 µg/g, except for in the central Delta, where mercury in carp was 0.16 ± 0.03 µg/g, more than half that of the north Delta and San Joaquin River. This spatial pattern was evident with many of the other species as well. Bluegill, channel catfish, redear sunfish, rainbow trout, and white catfish all had relatively low concentrations in the central Delta, but higher concentrations elsewhere. Bluegill and redear sunfish also had distinct spatial patterns in the Delta watershed, despite the smaller size of these species. Bluegill ranged from 0.08 µg/g in the central Delta to 0.17 µg/g in the northern Delta. The only region that appeared to have moderately high concentrations in bluegill was the Cosumnes–Mokelumne region, where mercury averaged 0.29 µg/g.

**Table 3**
Mean, upper and lower confidence intervals, and standard deviation of mercury, by region for species sampled in two or more regions. Fish size was constrained using length limits in Table 2.

| Region | Common name | Number of fish | Number of sites | Hg lower bound CI (95%) | Average Hg (µg/g) | Hg upper bound CI (95%) | Standard deviation |
|---|---|---|---|---|---|---|---|
| Central Delta | Bluegill | 56 | 13 | 0.060 | 0.082 | 0.104 | 0.040 |
| Cos-Mok Rivers | Bluegill | 11 | 3 | 0.071 | 0.289 | 0.506 | 0.192 |
| Eastern Drainages | Bluegill | 15 | 3 | 0.077 | 0.153 | 0.229 | 0.067 |
| Feather River | Bluegill | 14 | 3 | 0.070 | 0.161 | 0.253 | 0.081 |
| Northern Delta | Bluegill | 22 | 5 | 0.081 | 0.167 | 0.252 | 0.097 |
| Sacramento River | Bluegill | 33 | 7 | 0.091 | 0.144 | 0.197 | 0.072 |
| San Joaquin River | Bluegill | 46 | 11 | 0.102 | 0.132 | 0.162 | 0.050 |
| Central Delta | Channel catfish | 10 | 3 | 0.050 | 0.094 | 0.138 | 0.039 |
| Sacramento River | Channel catfish | 18 | 4 | 0.385 | 0.421 | 0.456 | 0.036 |
| San Joaquin River | Channel catfish | 17 | 4 | 0.116 | 0.169 | 0.222 | 0.054 |
| Western Drainages | Channel catfish | 26 | 3 | 0.144 | 0.211 | 0.278 | 0.059 |
| Central Delta | Common carp | 18 | 5 | 0.127 | 0.155 | 0.184 | 0.033 |
| Northern Delta | Common carp | 29 | 5 | 0.290 | 0.365 | 0.440 | 0.086 |
| Sacramento River | Common carp | 17 | 5 | 0.158 | 0.256 | 0.353 | 0.111 |
| San Joaquin River | Common carp | 61 | 13 | 0.239 | 0.304 | 0.370 | 0.121 |
| Sacramento River | Rainbow trout | 36 | 5 | 0.023 | 0.032 | 0.042 | 0.011 |
| San Joaquin River | Rainbow trout | 32 | 6 | 0.021 | 0.059 | 0.096 | 0.047 |
| Central Delta | Redear sunfish | 58 | 11 | 0.061 | 0.076 | 0.093 | 0.027 |
| Cos-Mok Rivers | Redear sunfish | 20 | 3 | 0.152 | 0.208 | 0.264 | 0.048 |
| Northern Delta | Redear sunfish | 36 | 6 | 0.086 | 0.113 | 0.139 | 0.033 |
| Sacramento River | Redear sunfish | 30 | 7 | 0.087 | 0.119 | 0.152 | 0.044 |
| San Joaquin River | Redear sunfish | 25 | 6 | 0.061 | 0.082 | 0.102 | 0.027 |
| Feather River | Sacramento sucker | 14 | 3 | 0.051 | 0.190 | 0.328 | 0.122 |
| Northern Delta | Sacramento sucker | 37 | 7 | 0.182 | 0.237 | 0.292 | 0.074 |
| Sacramento River | Sacramento sucker | 58 | 12 | 0.129 | 0.176 | 0.223 | 0.083 |
| San Joaquin River | Sacramento sucker | 45 | 10 | 0.142 | 0.204 | 0.267 | 0.100 |
| Northern Delta | Striped bass | 17 | 3 | 0.210 | 0.409 | 0.609 | 0.176 |
| Sacramento River | Striped bass | 22 | 3 | 0.369 | 0.422 | 0.475 | 0.047 |
| San Joaquin River | Striped bass | 21 | 3 | 0.272 | 0.524 | 0.777 | 0.223 |
| Central Delta | White catfish | 33 | 7 | 0.097 | 0.119 | 0.141 | 0.030 |
| Northern Delta | White catfish | 38 | 5 | 0.163 | 0.304 | 0.445 | 0.161 |
| San Joaquin River | White catfish | 30 | 5 | 0.117 | 0.183 | 0.250 | 0.076 |

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Redear sunfish followed the same spatial pattern as the larger target species, although the differences were more subtle, consistent with redear sunfish being generally lower in mercury relative to the other species. As with bluegill, redear sunfish were generally lower in mercury (0.08–0.12 μg/g), except on the Cosumnes and Mokelumne Rivers. In this region, concentrations were nearly twice as high (0.21 μg/g).

### 3.3. Factors controlling spatial differences in fish mercury concentrations

Examining regional patterns of mercury in sport fish across the watershed has highlighted relatively low concentrations in the central Delta and relatively high concentrations in the Cosumnes and Mokelumne Rivers (Davis et al., 2008a). The Cosumnes floodplain has been indicated as a hot spot for mercury in sport fish, as numerous species of varying size and trophic level (particularly, largemouth bass, bluegill, and redear sunfish) have exhibited higher concentrations in this region. As a result, consumption advisories have recently been issued for consuming fish from the lower Cosumnes and Mokelumne rivers due to elevated methylmercury concentrations in largemouth bass and other commonly caught species (Klasing et al., 2006). Moreover, the highest mercury concentration observed in the study was in an individual black crappie collected from Cosumnes River in 2006 that measured 2.34 μg/g. With such high concentrations on the Cosumnes River, we suspect that factors such as habitat type, ambient sediment or water methylmercury concentration, or differences in prey availability, could explain the spatial difference compared to adjacent waters.

Due to the extensive mercury contamination in the Delta watershed, substantial effort has been recently devoted to better understand the cycling of methylmercury in sediments, water, and biota (e.g., Heim et al., 2007; Marvin-DiPasquale et al., 2007). To address the unexplained pattern of higher mercury concentrations in fish from the Cosumnes River and other tributaries relative to the central Delta, recent studies have aimed to identify the processes governing mercury transformation and trophic transfer in these systems. Cosumnes River is the last major, non-dammed river that flows directly into the Delta, with substantial densities of submerged aquatic vegetation and seasonally inundated floodplains. Franks Tract, on the other hand, is a permanently flooded island in the central Delta, with mostly non-vegetated open water habitat (California Department of Fish and Game, 1998). Heim et al. (2007) presented sediment methylmercury concentrations sampled from both systems during 1999–2000. Interestingly, these data suggest surface sediment methylmercury concentrations were higher in the central Delta (0.72 $\pm$ 0.68 ng/g dry weight) than in the Cosumnes River (0.10 $\pm$ 0.10 ng/g). Ecosystem type (i.e., vegetated marsh vs. open water) was found to explain a large degree of the variability (Heim et al., 2007), but did not completely account for the contrasting pattern in average concentrations.

Relationships between mercury in fish to wetland types and other landscape features have been of interest to water quality managers, particular in areas of the Delta where wetland restorations are currently planned (Melwani et al., 2007). A recent suite of studies conducted for the California Bay Delta Authority Ecosystem Restoration Program, aimed to identify the factors that may dictate habitat differences in mercury cycling (Marvin-DiPasquale et al., 2007). These studies indicated that unlike some other areas of the US, such as the Chesapeake Bay (Mason and Lawrence, 1999) and the Florida Everglades (Gilmour et al., 1998), sediment methylmercury concentrations did not readily explain mercury concentrations higher in the food web. Instead, factors such as bacterial activity, availability of reactive mercury species, and suspended sediment loads, determined regional differences in water column mercury and subsequent transfer up the food web (Marvin-DiPasquale et al., 2007). These factors likely play an important role in other systems highly influenced by mercury contamination as well, but perhaps not to the degree of the Sacramento–San Joaquin Delta. Consequently, sediment methylmercury concentrations observed in the Delta have not necessarily paralleled concentrations in higher trophic level fish (Heim et al., 2007; Davis et al., 2008a). These implications were recently summarized by Pickhardt et al. (2006) who showed higher methylmercury uptake and accumulation rates in redear sunfish from the Cosumnes River relative to Franks Tract that could have resulted from a combination of factors. Higher uptake of mercury in fish from Cosumnes River was associated with consistently lower dissolved organic carbon (DOC), potential differences in food web or growth rates, and differences in methylmercury availability, relative to Franks Tract (Pickhardt et al., 2006). Although results indicated dietary sources to be the principal contributor to final tissue burdens, further research is still needed to differentiate the direct effects of DOC from other mechanisms that result in high mercury concentrations in fish.

As with sediments, direct water-borne exposure to methylmercury by fish may also differ significantly among habitats and relate to accumulation higher in the food web. In contrast to Delta sediments, in a few cases, methylmercury concentrations in the water column have been shown to correlate well with mercury concentrations in fish (e.g., Sveinsdottir and Mason, 2005). Such correlations are probably due to higher aqueous concentrations entering the base of the food web, which leads to higher methylmercury uptake at each ascending level of the food web. However, current evidence is limited by the few studies that have measured mercury in both water and fish from the same locations. The Central Valley Regional Water Quality Control Board has been investigating this scenario by collecting monthly methylmercury water samples over the last few years from more than 10 sites around the Delta, many of which overlap with FMP sampling locations by design. Significant positive correlations between annually-averaged methylmercury concentrations in water to that in 350-mm largemouth bass have been shown for some of these sites (Wood et al., 2006). Although, the biochemical influences on mercury availability are very complicated and generally not well understood, recent studies (Marvin-DiPasquale et al., 2007) have contributed significantly in identifying the processes that may help to identify areas of concern for future management decisions with respect to mercury cleanup actions (Watras et al., 1998; Pickhardt et al., 2006).

Mercury accumulation in predator species is thought to be largely derived from consumption of contaminated invertebrates and fish prey (Hall et al., 1997; Pickhardt et al., 2006). Therefore, correlations between sport fish and prey fish mercury were expected to explain a significant portion of the spatial variation observed in the watershed. Preliminary results from a food web model for largemouth bass using data collected by this study as well as other sources (B.K. Greenfield, San Francisco Estuary Institute, Oakland, California, unpublished data) suggests that growth rate, consumption rate, and prey concentrations significantly affect spatial differences in mercury for adult largemouth bass. However, by varying various input parameters to the model, prey mercury in particular, was shown to have the most significant influence. Mercury in adult largemouth bass was significantly correlated to mercury in prey fish over a 9-month to 2-year time interval.

Largemouth bass are opportunistic predators, consuming any abundant invertebrate and fish prey of appreciable size (Moyle, 2002). In a diet study of more than 100 largemouth bass collected from two sites in the Delta in 2001 and 2003, crayfish, gobies, juvenile sunfish, and silversides were found to be the most common prey items (M. Norbriga, Department of Water Resources, Davis, California, unpublished data). Linear regression was

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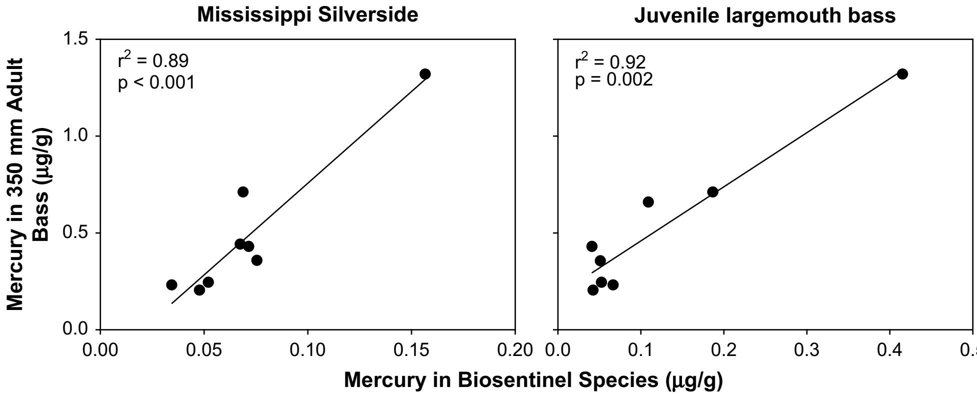


**Fig. 5.** Relationship between average mercury concentration in Mississippi silverside (left) and juvenile largemouth bass (right) to 350-mm adult largemouth bass at co-located sites sampled in the Project.

employed here to examine whether statistical correlations could be determined between mercury in whole prey fish (D. Slotton, University of California-Davis, unpublished data) and coexisting, size-standardized adult largemouth bass across eight sites sampled in the Project. Two biosentinel species were selected for the evaluation; Mississippi silverside (*Menidia beryllina*, the most widespread small fish species in the Delta) and juvenile largemouth bass, for comparison to adults of the same species. Statistical analysis indicated significant, positive relationships ($r^2 \sim 0.9$, $p < 0.05$) to adult largemouth bass concentrations for both biosentinel fish species (Fig. 5). Removal of the highest data point in each plot did not alter the statistical significance of the regressions. Previously, few studies have demonstrated such a relationship, likely due to the complex interactions between direct and indirect accumulation of mercury in predatory fish (e.g., Sveinsdottir and Mason, 2005). However, prior studies have not measured mercury in small fish species as intensively as was performed for this study. These results suggest that adult bass in the Delta watershed are reasonably good indicators of mercury entering the base of the food web, as their concentrations are highly correlated to that in primary consumers. The significant correlation of prey concentrations averaged over a three-year sampling period may also indicate that this time interval provides a reasonable approximation of the dietary exposure history for largemouth bass.

To examine whether consistent relationships existed among species, in order for our results in largemouth bass to be extrapolated, mercury concentrations averaged by site were compared to other sport fish. The data used for this evaluation included species that were sampled at 10 or more of the same sites. Largemouth bass mercury concentrations were statistically significant ($p \ll 0.05$) and positively correlated with concentrations in six other fish species examined, except Sacramento sucker (Table 4). This suggests that a significant proportion of the variation in mercury concentration in many of the species sampled can be estimated using concentrations in largemouth bass, which may have implications for future studies of mercury in sport fish.

Based on the detailed information on mercury contamination and spatial trends obtained through this study, the FMP has provided the basis upon which future sport fish sampling designs may be developed. This study has revealed the importance of characterizing different trophic levels of the food web, rather than for the need to sample all abundant fish species from a watershed to characterize patterns in contamination. The regional approach to evaluating fish mercury concentrations also proved successful, with generally consistent mercury concentrations apparent across similar habitats. As a result, future studies of sport fish mercury concentrations may seek to optimize the efficiency of their sampling by selecting representative species for different trophic levels and by considering existing information on expected high and low areas for exposure in a watershed. In addition, the statistical analysis indicated that wide ranges (>130 mm) in total length of largemouth bass, and sample sizes of more than eight largemouth bass per site are necessary to build robust length:mercury relationships to evaluate spatial patterns. Future efforts can use the extensive dataset generated in this study in power analysis to determine the necessary sample sizes required to detect spatial and temporal trends of fish mercury concentrations.

### 3.4. Temporal comparison of mercury concentrations

The third main purpose of sport fish sampling was to characterize inter-annual variation in sport fish mercury. Statistical analysis of mercury concentrations in 350-mm largemouth bass from 2000, 2005, and 2007 did not reveal a discernible trend, but a consistent pattern of inter-annual fluctuation was evident (Fig. 6). Mercury in largemouth bass was not significantly different between 2000 and 2007, but 2005 was on average 0.13 µg/g lower than each of the other years. Note that the confidence intervals of each mean value may appear to span the same range, but in-fact do differ by a small proportion, indicating similar variability in largemouth bass standardized mercury across sites. The lower concentrations observed across sites in 2005 may be due to factors such as water chemistry or largemouth bass life-history. For example, the largemouth bass modeling effort has been evaluating the role that seasonal variation and life-history of largemouth bass play in explaining the concentrations observed in the region. Preliminary results suggest that up to 75% of the bass concentrations could be explained by higher prey mercury concentrations occurring 9-months to 2-years prior (B.K. Greenfield, San Francisco Estuary Institute, Oakland, California, unpublished data). However, differences in age–weight ratios were also apparent, with fish in 2005 being heavier at a given age than fish from 2000 to 2007 (Davis

**Table 4**
Relationship in mercury concentrations between largemouth bass and other frequently sampled fish species. All relationships were positive.

| Species compared to Largemouth bass | *N* | $r^2$ | *F*-ratio | *p*-Value |
|---|---|---|---|---|
| Sacramento sucker | 20 | 0.01 | 0.13 | 0.72 |
| White catfish | 19 | 0.57 | 22.1 | 0.0002 |
| Bluegill | 38 | 0.46 | 30.5 | < 0.0001 |
| Channel catfish | 16 | 0.52 | 15.1 | 0.002 |
| Common carp | 26 | 0.46 | 20.1 | 0.0002 |
| Redear sunfish | 29 | 0.46 | 22.9 | 0.0001 |

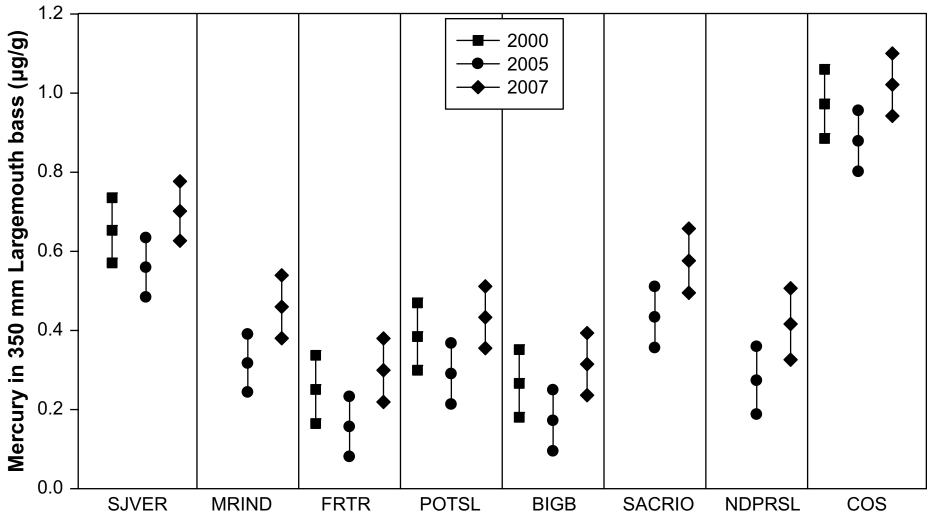


**Fig. 6.** Predicted mercury concentrations (mean ± 95% confidence intervals) for 350-mm largemouth bass at eight sites sampled by the Project in 2005 and 2007, and by Davis et al. (2008a,b). Refer to Table 1 for site abbreviations.

et al., 2008a). Therefore, growth dilution may also have contributed to the lower mercury concentrations predicted for largemouth bass in 2005. Negative association of growth rate with tissue mercury concentrations has been suggested in the literature (Simoneau et al., 2005), but remains an area of on-going research.

Mercury concentrations in striped bass in San Francisco Bay have shown similar temporal patterns to largemouth bass. Striped bass sampled over a period of 33 years (1970–2003) have shown some inter-annual fluctuations, but no overall trend (Davis et al., 2006). These findings are consistent with the long residence time of mercury in the Bay and Delta (Conaway et al., 2007). Thus, the available information suggests that mercury concentrations in sport fish in some regions of the Delta watershed may remain elevated for decades, in the absence of significant management actions to reduce accumulation in the food web. Clearly, continued monitoring of mercury in sport fish of the watershed will be essential to efforts to address this widespread water quality problem.

## 4. Conclusions

During the three years of study in the CALFED Fish Mercury Project, the main objective of characterizing mercury concentrations to assess health risks from consuming contaminated fish was achieved using data from frequently caught species in the watershed. After three years of intensive sampling in the Sacramento–San Joaquin Delta, largemouth bass was consistently the most contaminated of the target species, followed by striped bass, common carp and catfish. Of all species sampled, redear sunfish, bluegill, and rainbow trout were identified as having generally low concentrations and potentially being good alternatives for human consumption. It is important to remember, however, that these conclusions only pertain to methylmercury, given that organics analyses were not conducted on these samples.

The second main objective of the Project was to characterize spatial trends in the piscine food web to determine mercury accumulation. Overall, the spatial patterns in mercury observed during 2005–2007 were consistent with patterns documented by previous studies in the Delta. Davis et al. (2008a,b) reported relatively high concentrations in largemouth bass from both the Cosumnes and Mokelumne Rivers in 1999 and 2000. Locations on the Feather, Sacramento, and San Joaquin Rivers were also noted in that study to be elevated over concentrations in the central Delta. In the present study, large, piscivorous species exhibited the greatest spatial variation, with mercury concentrations highest at locations on the lower portions of the Sacramento and San Joaquin Rivers, the north Delta, Cosumnes and Mokelumne rivers. Lower concentrations were found in numerous species on the higher reaches of the San Joaquin River and the central Delta. The largest spatial difference in mercury was found for largemouth bass, which differed by 0.6 µg/g between the Cosumnes River and the central Delta. This variation in mercury may be explained by a number of factors, including exposure to methylmercury concentrations in water and prey. Furthermore, integration of the biosentinel fish data with that of largemouth bass indicated relatively strong prey–predator mercury relationships across habitats. As a result, largemouth bass have shown to be good indicators of mercury entering the Delta food web, although they may not be as sensitive to inter-annual trends as small prey fish. Furthermore, largemouth bass mercury was shown to correlate with mercury concentration in other sport fish species. This suggests that selection of species for characterizing mercury concentration could be optimized in future studies using information on trophic level, size, and distribution in the watershed.

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## Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envpol.2009.05.013.

## References

Becker, G.C., 1983. Fishes of Wisconsin. University of Wisconsin Press, Madison.
Bloom, N.C., 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Canadian Journal of Fisheries & Aquatic Sciences 49, 1010–1017.
Burnham, K.P., Anderson, D.R., 2002. Model Selection and Multimodel Inference: a Practical Information-Theoretic Approach, second ed.. Springer Science, New York, NY.
California Department of Fish and Game, 1998. California Central Valley Wetlands and Riparian GIS Database. http://www.delta.dfg.ca.gov/GIS/erip/dnload_default.asp.
Choi, B.H., 1990. Effects of methylmercury on the developing brain. In: Suzuki, T., Imura, N., Clarkson, T.W. (Eds.), Advances in Mercury Toxicology. Plenum, New York, NY, pp. 315–337.
Conaway, C.H., Ross, J.R.M., Looker, R., Mason, R.P., Flegal, A.R., 2007. Decadal mercury trends in San Francisco Bay sediments. Environmental Research 105, 53–66.
Davis, J.A., May, M.D., Ichikawa, G., Crane, D., 2000. Contaminant Concentrations in Fish from the Sacramento–San Joaquin Delta and Lower San Joaquin River, 1998. San Francisco Estuary Institute, Richmond, CA, 52 pp.
Davis, J.A., Hunt, J.A., Greenfield, B.K., Fairey, R., Sigala, M., Crane, D.B., Regalado, K., Bonnema, A., 2006. Contaminant Concentrations in Fish from San Francisco Bay, 2003. San Francisco Estuary Institute, Oakland, CA.
Davis, J.A., Greenfield, B.K., Ichikawa, G., Stephenson, M., 2008a. Mercury in sport fish from the Sacramento–San Joaquin delta region, California. Science of the Total Environment 391, 66–75.
Davis, J.A., Melwani, A.R., Bezalel, S.N., Ichikawa, G., Bonnema, A., Lamerdin, C., Heim, W.A., Crane, D., Stephenson, M., 2008b. Contaminants in Sport Fish of California Lakes and Reservoirs. San Francisco Estuary Institute, Oakland, CA.
Gassel, M., Brodberg, R.K., Klasing, S., Roberts, S., 2006. Draft Safe Eating Guidelines for Fish and Shellfish from the San Joaquin River and South Delta (Contra Costa, San Joaquin, Stanislaus, Merced, Madera, and Fresno Counties. OEHHA, Sacramento, CA, 130 pp.
Gilmour, C.C., Riedel, G.S., Ederington, M.C., Bell, J.T., Benoit, J.M., Gill, G.A., Stordal, M.C., 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry 40, 327–345.
Hall, B.D., Bodaly, R.A., Fudge, R.J.P., Rudd, J.W.M., Rosenberg, D.M., 1997. Food as the dominant pathway of methylmercury uptake by fish. Water, Air, and Soil Pollution 100, 13–24.
Heim, W.A., Coale, K.H., Stephenson, M., Choe, K.Y., Gill, G.A., Foe, C., 2007. Spatial and habitat-based variations in total and methyl mercury concentrations in surficial sediments in the San Francisco bay-delta. Environmental Science & Technology 41, 3501–3507.
Klasing, S., Brodberg, R.K., 2008. Development of Fish Contaminant Goals and Advisory Tissue Levels for Common Contaminants in California Sport Fish: Chlordane, DDTs, Dieldrin, Methylmercury, PCBs, Selenium, and Toxophene. OEHHA, Sacramento, CA, 115 pp.
Klasing, S., Gassel, M., Roberts, S., Brodberg, R.K., 2006. Draft Safe Eating Guidelines for Fish and Shellfish from the Lower Cosumnes and Lower Mokelumne Rivers (Sacramento and San Joaquin Counties). OEHHA, Sacramento, CA, 130 pp.
Littell, R.C., Milliken, G.A., Stroup, W.W., Wolfinger, R.D., 1996. SAS System for Mixed Models. SAS Institute, Inc., Cary, NC.
Marvin-DiPasquale, M., Stewart, A.R., Fisher, N.S., Pickhardt, P., Mason, R.P., Heyes, A., Windomham-Meyer, L., 2007. Evaluation of Mercury Transformations and Trophic Transfer in the San Francisco Bay/Delta: identifying Critical Processes for the Ecosystem restoration Program. Final Report for project # ERP-02-P40, Prepared by U.S. Geological Survey, University of Connecticut, and SUNY Stony brook, Submitted to the California Bay Delta Authority, Sacramento, CA. 40 pp.
Mason, R.P., Lawrence, A.L., 1999. Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore harbor and Chesapeake Bay, Maryland, USA. Environmental Toxicology and Chemistry 18, 2438–2447.
Melwani, A.R., Bezalel, S.N., Grenier, J.L., Hunt, J.A., Robinson, A.H., Davis, J.A., 2007. The Relationship Between Landscape Features and Sport Fish Mercury in the Sacramento–San Joaquin Delta Watershed. SFEI Contribution 534. San Francisco Estuary Institute, Oakland, CA.
Mergler, D., Anderson, H.A., Chan, L.H.M., Mahaffey, K.R., Murray, M., Sakamoto, M., Stern, A.H., 2007. Methylmercury exposure and health effects in humans: a worldwide concern. Ambio 36, 3–11.
Moyle, P.B., 2002. Inland Fishes of California. University of California Press, Berkeley, CA.
OEHHA, 1994. Health Advisory on Catching and Eating Fish: Interim Sport Fish Advisory for San Francisco Bay and Delta Region. OEHHA, Sacramento, CA. http://www.oehha.org/fish/general/sfbaydelta.html.
Pickhardt, P.C., Stepanova, M., Fisher, N.S., 2006. Contrasting uptake routes and tissue distributions of inorganic and methylmercury in mosquitofish (*Gambusia affinis*) and redear sunfish (*Lepomis microlophus*). Environmental Toxicology and Chemistry 25, 2132–2142.
Puckett, H.M., van Buuren, B.H., 2000. Quality Assurance Project Plan for the CALFED Project: an Assessment of Ecological and Human Health Impacts of Mercury in the Bay-Delta Watershed. California Department of Fish and Game, Monterey, CA, 46 pp.
Silver, E., Kaslow, J., Lee, D., Tan, M.L., Weis, E., Ujihara, A., 2007. Fish consumption and advisory awareness among low-income women in California's Sacramento–San Joaquin Delta. Environmental Research 104, 410–419.
Simoneau, M., Lucotte, M., Garceau, S., Laliberte, D., 2005. Fish growth rates modulate mercury concentrations in walleye (*Sander vitreus*) from eastern Canadian lakes. Environmental Research 98, 73–82.
Sveinsdottir, A., Mason, R.P., 2005. Factors controlling mercury and methylmercury concentrations in largemouth bass (*Micropterus salmoides*) and other fish from Maryland reservoirs. Archives of Environmental Contamination and Toxicology 49, 528–545.
Tremblay, G., Doyon, J., Schetagne, R., 1995. Environmental Monitoring Network of the La Grande Complex. Monitoring of Mercury Levels in Fish: Approach and Methods. Direction Principale Communications et Environnement Groupe-conseil Genivar Inc., 33 + appendices pp
Tremblay, G., Legendre, P., Doyon, J., Verdon, R., Schetagne, R., 1998. The use of polynomial regression analysis with indicator variables for interpretation of mercury in fish data. Biogeochemistry 40, 189–201.
US EPA, 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. EPA-823-B-00-007. In: Fish Sampling and Analysis, third ed, vol. 1. US Environmental Protection Agency, Washington, DC.
USGS, 2000. Mercury Contamination from Historic Gold Mining in California. Fact Sheet FS-061-00. US Geological Survey, Sacramento, CA.
van Buuren, B.H., 2006. The California Bay-Delta Authority Mercury Studies Quality Assurance Program Intercomparison Study 2, November 2005. van Buuren Consulting, LLC, Seattle, WA, 44 pp.
Watras, C.J., Back, R.C., Halvorsen, S., Hudson, R.J.M., Morrison, K.A., Wente, S.P., 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Science of the Total Environment 219, 183–208.
Wiener, J.G., Gilmour, C.C., Krabbenhoft, D.P., 2003. Mercury Strategy for the Bay-Delta Ecosystem: Unifying Framework for Science, Adaptive Management, and Ecological Restoration. CALFED Bay-Delta Mercury Project, Sacramento, CA.
Wood, M., Foe, C., Marquis, G., Cooke, J., 2006. Sacramento–San Joaquin Delta Estuary TMDL for Methyl and Total Mercury, Staff Report, Draft Report. Regional Water Quality Control Board, Central Valley Region, Rancho Cordova, CA.