## Contaminant Concentrations in Fish

 from the Sacramento-San Joaquin Delta and Lower San Joaquin River 1998

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September 2000

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## Acknowledgments

Funding for this study was arranged by Bill Jennings (Deltakeeper) and Chris Foe (Central Valley Regional Water Quality Control Board). Chris Foe, Bob Brodberg (Office of Environmental Health Hazard Assessment), and Bill Jennings were actively engaged in all phases of the study, from sampling design to review of a draft of this report.

Staff of the Moss Landing Marine Laboratory, including Mark Pranger, Alex Cully, Autumn Bonnema, and Jon Goetzl, collected the fish samples. Jack Linn (California Department of Fish and Game) provided guidance and assistance in fish collections. Moss Landing Marine Lab staff (Jon Goetzl and Lisa Berrios) also performed trace element measurements. Kathleen Regalado, Laurie Smith, Abdou Mekebri, Gary Munoz, and Jim McCall of the California Department of Fish and Game Water Pollution Control Laboratory performed the trace organic analyses. Ray Schaffter (California Department of Fish and Game) arranged for age determination of largemouth bass.

Henry Lee (U.S. EPA) reviewed a draft of this report.
Liz Hartman and Frank Leung (SFEI) assisted with contract management.
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Cover created by Michael May.

This report should be cited as:
Davis, J.A., M.D. May, G. Ichikawa, and D. Crane. 2000. Contaminant Concentrations in Fish from the Sacramento-San Joaquin Delta and Lower San Joaquin River, 1998. San Francisco Estuary Institute, Richmond, CA.

## Executive Summary

In spite of the popularity of the Delta as a fishing location, human health concerns raised beginning in 1971, the existence of a consumption advisory for the Bay, and recent concern over fish tissue contamination in the Sacramento River watershed, very little systematic sampling has been conducted in the Delta to evaluate human health risks associated with chemical contamination of fish tissue. This report documents the most systematic, comprehensive survey of chemical contamination of fish in the Delta yet performed.

The objectives of this study were, in order of priority:

1. To conduct a pilot study to determine whether mercury, organochlorine pesticides, and PCBs occur in fish that are being used as human food in the Delta at concentrations of potential human health concern.
2. To measure contaminant levels in fish to begin to track long-term trends and evaluate the effectiveness of management efforts.
3. To determine spatial patterns in contamination in the Delta.
4. To provide data that are useful in assessing the ecological hazards of mercury and organochlorines in organisms at high trophic levels.

Sampling was performed in late summer 1998, and focused on largemouth bass and white catfish, two abundant and popular sport fish species. Measured concentrations were compared to screening values, which are defined as concentrations of target analytes in fish or shellfish tissue that are of potential public health concern. Exceedance of screening values should be interpreted as an indication that more intensive site-specific monitoring and/or evaluation of human health risk should be conducted.

Mercury concentrations were frequently above the screening value. One half of the largemouth bass and white catfish samples analyzed exceeded the mercury screening value ( 11 of 19 largemouth bass and 4 of 11 white catfish). Consistent regional variation has been observed in both species, with the higher concentrations and more screening value exceedances in the lower San Joaquin River watershed, and generally low concentrations in the central Delta. Concentrations of PCBs were above the screening value in $30 \%$ of the samples ( 3 of 19 largemouth bass and 6 of 11 white catfish). Available data suggest that PCBs are elevated in localized hotspots rather than on a regional basis. Concentrations of DDT exceeded the screening value in $23 \%$ of the samples ( 1 of 19 largemouth bass and 6 of 11 white catfish). All of the samples above the DDT screening value were obtained from the south Delta or lower San Joaquin River watershed. Other chemicals which are possible concerns in the Delta include dieldrin, toxaphene, arsenic, PAHs, and dioxins.

The following recommendations are based on these findings: 1) Long term monitoring should be conducted to track trends in contaminants of concern in sport fish relative to screening values; 2) Further fish sampling should be conducted in the San Joaquin River watershed to characterize human health concerns related to chemical contamination; and 3) A fishery resource use study should be conducted in the Delta and Central Valley.


Figure 1. Sampling locations for this study. SRWP sampling locations are also shown.

## Introduction

In 1969, as the scope of worldwide environmental contamination due to mercury was first being discovered, two striped bass from the Delta were found to have 700 $\mathrm{ng} / \mathrm{g}$ mercury in their muscle tissue. In 1970, as a result of this finding, an Interagency Committee was created to evaluate mercury contamination in California (California State Department of Public Health 1971). The Committee assembled existing data and initiated further studies of mercury in sport fish, commercial fish, game birds, water, and sediments. In samples collected between April and July 1970, 55 of 102 fish collected in the Delta region were higher than $500 \mathrm{ng} / \mathrm{g}$. This included 42 striped bass weighing over 4 pounds that were all higher than $500 \mathrm{ng} / \mathrm{g}$. In 1971, based on these studies, a human health advisory was issued for the Delta advising pregnant women and children not to consume striped bass.

In 1993 the advisory for the Delta was revised by the California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA) upon review of more mercury data for striped bass. The revised advisory included size-specific consumption advice for adults, children 6-15 years, and pregnant women and children under age 6.

Recent studies in the Bay-Delta watershed have also found concentrations of mercury and other chemicals that are of potential human health concern in striped bass and other popular sport fish species. Extensive sampling was conducted in San Francisco Bay in 1994 and 1997 (SFBRWQCB 1995, Fairey et al. 1997, SFEI 1999). In response to the 1994 results, an interim fish consumption advisory was issued for the Bay-Delta, due to concern over human exposure to methylmercury, PCBs, organochlorine pesticides, and dioxins (OEHHA 1994). This advisory is still in place. The current version of the advisory states that:

- Adults should limit consumption of Bay sport fish, and striped bass and sturgeon from the Delta to, at most, two meals per month.
- Adults should not eat any striped bass over 35 inches ( 89 cm ).
- Pregnant women or women that may become pregnant or are breastfeeding, and children under 6 should not eat more than one meal per month, and should not eat any meals of shark over 24 inches ( 61 cm ) or striped bass over 27 inches ( 69 cm ).

Sport fish have also been sampled in the Sacramento River under the Sacramento River Watershed Program (SRWP) since 1997 (Larry Walker Associates 2000). This annual sampling program includes two locations in the northern Delta and several others just upstream of the Delta in the lower Sacramento River watershed. Concentrations of mercury in white catfish and largemouth bass in this program have frequently been above screening values and have been comparable to concentrations that led to the interim advisory for the Bay. Concentrations of PCBs, dieldrin, DDT, and toxaphene above screening values have also been found in this Program.

In spite of the popularity of the Delta as a fishing location, the concerns raised in the 1971 report (California State Department of Public Health 1971), the existence of the consumption advisory for the Bay, and recent concern over fish tissue contami-
nation in the Sacramento River watershed, very little sampling has been conducted in the Delta since 1971 to evaluate human health risks associated with chemical contamination of fish tissue. This report documents the most systematic, comprehensive survey of chemical contamination of fish in the Delta yet performed.

The objectives of this study were, in order of priority:

- To conduct a pilot study to determine whether mercury, organochlorine pesticides, and PCBs occur in fish that are being used as human food in the Delta at concentrations of potential human health concern.
- To measure contaminant levels in fish to begin to track long-term trends and evaluate the effectiveness of management efforts.
- To determine spatial patterns in contamination in the Delta.
- To provide data that are useful in assessing the ecological hazards of mercury and organochlorines in organisms at high trophic levels.

Sampling in 1998 for the SRWP and the Delta Study had similar objectives, employed identical methods, and focused on the same species. The data from these two efforts are therefore directly comparable and can be combined to provide a picture of chemical contamination in sport fish that covers a large portion of the Central Valley. SRWP data from 1997 and 1998 are incorporated into the analysis presented in this report to provide this broad context. The State Water Resources Control Board's Toxic Substances Monitoring Program (TSMP) is another primary source of data on sport fish contamination in the Central Valley. The TSMP began measurement of toxic chemicals in freshwater fish and shellfish throughout California in 1978 and has continued to the present (Rasmussen 1997). Although the species and locations sampled by the TSMP have fluctuated, the data generated by this program collectively provide a fragmented yet informative overview of fish tissue contamination in California's freshwater habitats, including the Delta. TSMP data are also incorporated into the discussion of spatial and temporal trends in this report.

The primary source of funds for this study was an environmental mitigation fund contributed by the Port of Stockton as part of a federal court settlement agreement. The Deltakeeper had filed a lawsuit alleging Clean Water Act violations by the Port, and the mitigation fund was one component of the out-of-court settlement agreement. Additional funds were provided by the Central Valley Regional Water Quality Control Board.

## Methods

Largemouth bass (Micropterus salmoides) and white catfish (Ictalurus catus) were selected as the primary target species for this study. These popular sport fish species are resident and relatively abundant in the Delta (CDFG 1999). These species are also at a high trophic level, a characteristic which favors accumulation of mercury and organochlorines. Furthermore, since largemouth bass feed in the water column and white catfish are more bottom-oriented foragers, these two species capture different routes of exposure and accumulation as recommended in U.S. EPA guidance on surveys of fish tissue contamination (U.S. EPA 1995).

Largemouth bass are primarily piscivores; occasionally populations prefer crayfish, tadpoles, or frogs (Moyle 1976). The target size range for largemouth bass was $305-438 \mathrm{~mm}(12-17.25 \mathrm{in})$. This range was selected based on the lower legal limit and U.S. EPA (1995) guidance that the smallest fish in a composite be no less than $75 \%$ of the largest. Largemouth bass in this size range were from 2 to 6 years old. A literature search did not yield any information on the mobility of largemouth bass in the Delta. A recent report (Lee 2000) described the growing popularity of largemouth bass fishing tournaments in the Delta, which results in the capture and relocation of thousands of largemouth annually. These relocations may introduce additional variance in contaminant concentrations at sampling locations in the Delta.

White catfish are opportunistic, carnivorous bottom feeders. In the Delta they feed primarily on amphipods and shrimp, but also eat fish and large invertebrates (Moyle 1976). The target size range for white catfish was 229-330 mm (9-13 in). This range was selected based on the size of fish caught in TSMP sampling and U.S. EPA guidance on compositing. This range brackets the mean length of white catfish ( 258 mm ) measured in August of 1997 by the Resident Fishes Monitoring Program (CDFG 1999). The white catfish population in the Delta is one of the slowest growing populations of this species known. Based on information presented in Moyle (1976), fish in the target range would be between 4 and 7 years old. The slow growth rate of white catfish in the Delta (Moyle 1976) might lead to relatively high mercury concentrations relative to length in this region compared to white catfish populations in other regions, as observed in a study comparing sympatric populations of dwarf and normal lake whitefish (Doyon et al. 1998). A literature search did not yield any information on the mobility of white catfish in the Delta.

Fish samples were collected between August 10 and September 11, 1998. Fish were collected with an electrofisher boat and with fyke nets. Total length (longest length from tip of tail fin to tip of nose/mouth) was measured in the field. Information on bycatch, including species and approximate numbers, was recorded. A detailed sampling report is available from SFEI.

Sampling locations were selected to include known fishing areas and to provide broad geographic coverage (Figure 1). Published information on fish catch and consumption for the Delta were not available, so location selection had to be based on anecdotal information on fishing locations. The sampling design called for collection of both largemouth bass and white catfish at each of the 19 locations. White catfish could not be collected at 8 locations. At three of these locations brown bullhead (Ictalurus nebulosus) was collected as an alternate, following the same protocol for size as used for white catfish.

The target number of fish for each composite was five. Target species that were larger than the specified size ranges were kept if they were caught. At sites where large largemouth bass were caught, fish were analyzed individually in order to investigate relationships between length, age, and mercury and lipid and organics. Individual largemouth bass were also analyzed at one location (San Joaquin River at Vernalis) where 10 fish were caught (with the original intent of forming two composites of five fish). In calculating summary statistics, the individual results from these three locations were averaged to provide values that could be compared to the composites from the other locations. White catfish and brown bullhead were analyzed as composites of
five fish. Duplicate composites of white catfish were analyzed at one location: San Joaquin River at Vernalis.

The clam Corbicula fluminea was collected at three locations (Port of Stockton near New Mormon Slough, Middle River at Bullfrog, and Sacramento River at Rio Vista) for evaluation of human health concerns from clam consumption. One composite sample was prepared for each location. The number included in each composite ranged from 24 to 68 individuals; the average length in each composite ranged from 25 to 33 mm . Mercury was analyzed in each of these samples. Organics were analyzed in two of the three samples.

Sampling and chemical analysis was performed in accordance with the QAPP for the Regional Monitoring Program for San Francisco Bay (Lowe et al. 1999). After capture, fish were wrapped in chemically cleaned Teflon sheeting, placed in Ziploc bags, and frozen on dry ice for transportation to the laboratory. Dissection and tissue sample preparation were performed following U.S. EPA (1995) guidance using noncontaminating techniques in a clean room environment. Fish were thawed and weighed prior to dissection. Scales were removed from largemouth bass prior to filleting. Skin was removed from white catfish and black bullhead. Approximately 40 g of fillet were taken from each fish, yielding a total of approximately 200 g for each composite sample. Approximately 180 g were placed in a clean jar for organic analysis, and 20 g were stored in a clean jar for mercury analysis.

Trace elements were analyzed by the Moss Landing Marine Laboratory. Samples for trace element analysis were digested in a nitric:perchloric acid mixture. Mercury was analyzed using a Perkin Elmer Flow Injection Mercury System (FIMS). Continuing calibration checks were run after every 10 samples. Blanks, standard reference materials (DORM-1: dogfish muscle and liver), and matrix spikes were run with each set of samples for fish. Arsenic and selenium were analyzed with a Perkin Elmer ELAN 6000 ICP-MS. NRC SRM 2976 was used for arsenic and selenium measurements. QA/QC results all met the data quality objectives of the QAPP. A full QA and data report on the trace element analysis is available from SFEI.

Trace organics were analyzed by the California Department of Fish and Game Water Pollution Control Laboratory. A 10 g sample of homogenate for trace organic analysis was extracted with a 50/50 mixture of acetone/dichloromethane in a Dionex Accelerated Solvent Extractor (ASE 200). Extract cleanup was then performed using gel permeation chromatography. Twenty percent of each extract was removed and weighed for percent lipid determination. For organochlorine analysis, cleaned up extract was then fractionated into four fractions using Florisil. Each fraction was then analyzed using dual column high resolution gas chromatography with a HewlettPackard 6890 plus GC with electron capture detection, with two $60 \mathrm{~m}, 0.25 \mathrm{~mm}$ i.d., $0.25 \mu \mathrm{~m}$ film thickness columns (DB-5 and DB-17: J\&W Scientific). Extracts for PAH analysis were cleaned up using activated silica gel/alumina and analyzed on a Varian 4D Ion Trap GCMS using a $60 \mathrm{~m}, 0.25 \mathrm{~mm}$ i.d., $25 \mu \mathrm{~m}$ film thickness DB5MS capillary column. Reference materials from the International Atomic Energy Agency (IAEA) (fish homogenate MA-B-3/OC and mussel MA-M-2/OC) and the National Institute of Standards and Technology (SRM 1588a: organics in cod liver oil) were used in QA evaluation. Overall, the reported data were of excellent quality. Minor exceedance of data quality objectives occurred for particular analytes, but had
minimal impact on the data presented in this report. A full QA and data report for the trace organics is available from SFEI.

Scales were removed from largemouth bass prior to dissection to allow estimation of age. Scale aging was performed for the largemouth bass analyzed as individuals by Ray Schaffter of the DFG Bay-Delta unit in Stockton. Consensus from three readers was obtained on 20 of 24 samples.
U.S. EPA (1995) defines screening values as concentrations of target analytes in fish or shellfish tissue that are of potential public health concern. Exceedance of screening values should be taken as an indication that more intensive site-specific monitoring and/or evaluation of human health risk should be conducted. Screening values were taken from OEHHA (1999) or calculated following U.S. EPA (1995) guidance and using the consumption rate ( $21 \mathrm{~g} /$ day) employed by OEHHA (1999).

Statistical analyses were performed using SAS (SAS Institute, 1990). All data are presented in wet weight unless otherwise noted. Summary statistics are presented as medians, which provide an indication of central tendency regardless of the distribution of the data. Appendix A contains tables with the complete dataset.

## Results and Discussion

## Mercury

## Introduction

Mercury is the primary concern behind the past and present advisories for consumption of fish from the Delta. In humans, mercury is a neurotoxicant, and is particularly hazardous for fetuses and children as their nervous systems develop (OEHHA, 1994b). Mercury can cause many types of problems in children, including mental impairment, impaired coordination, and other developmental abnormalities. In adults, mercury has neurotoxic effects that include decrements in motor skills and sensory ability at comparatively low doses, to tremors, inability to walk, convulsions and death at extremely high exposures. Similarly, in wildlife species mercury can cause damage to nervous, excretory, and reproductive systems, and early life stages are most sensitive (Wolfe et al. 1998).

Mercury exists in the environment in a variety of chemical forms. The most important form of mercury in the aquatic environment is methylmercury, which is readily accumulated by biota and transferred through the food web. Most of the mercury that accumulates in fish tissue is methylmercury (U.S. EPA, 1995). Methylmercury is also the form of mercury of greatest toxicological concern at concentrations typically found in the environment. The principal sources of mercury to aquatic ecosystems in northern California are historic mercury and gold mining sites, fossil fuel combustion, trace impurities in products such as bleach, and direct use of the metal in applications such as thermometers and dental amalgam (SFBRWQCB, 1998). Fish, especially long-lived predators at the top of the food web, accumulate high concentrations of mercury and are fundamental indicators of the human and wildlife health risks associated with mercury in aquatic ecosystems.

## Analytical considerations

The screening value for mercury, $0.3 \mu \mathrm{~g} / \mathrm{g}$ wet weight, applies to methylmercury. Because of the higher cost of methylmercury analysis and data indicating that most mercury in fish tissue is present as methylmercury, U.S. EPA (1995) recommends that total mercury be measured in fish contaminant monitoring programs and the conservative assumption made that all mercury is present as methylmercury in order to be most protective of human health. Total mercury was measured in these samples.

The mercury concentrations in fish were easily measured with the analytical methods employed. The minimum concentration in field samples was $12 \mathrm{ng} / \mathrm{g}$ wet, 12 times higher than the method detection limit ( $1 \mathrm{ng} / \mathrm{g}$ wet).

## Data distribution and summary statistics

Largemouth bass had the highest median mercury concentration ( $350 \mathrm{ng} / \mathrm{g}$ ) (Table 1, Figure 2). In composite samples, concentrations ranged from a low of 84 $\mathrm{ng} / \mathrm{g}$ in Smith Canal to a high of $670 \mathrm{ng} / \mathrm{g}$ at Stanislaus River upstream of Caswell State Park. Eleven of nineteen locations had concentrations above the $300 \mathrm{ng} / \mathrm{g}$ screening value (Table 2, Figure 3). Eight locations in the central and southern Delta had concentrations below the screening value. Locations further upstream on both the Sacramento and San Joaquin rivers were all above the screening value (Figure 3). Concentrations in the fish analyzed individually (from three locations) ranged from a low of $240 \mathrm{ng} / \mathrm{g}$ (Sycamore Slough) to a high of $700 \mathrm{ng} / \mathrm{g}$ in a large fish (also Sycamore Slough).

Other species were analyzed solely as composites. White catfish had slightly lower concentrations than largemouth bass, with a median of $290 \mathrm{ng} / \mathrm{g}$ (Table 1, Figure 2). Concentrations in white catfish composites ranged from a low of $85 \mathrm{ng} / \mathrm{g}$ at Smith

Table 1. Summary statistics by species for trace elements and selected organic contaminants. Data are medians. All units $\mathrm{ng} / \mathrm{g}$ wet weight unless indicated. For median calculation, $N D$ was set equal to zero. $N D=$ not detected.

| Species |  |  |  | $\begin{aligned} & \text { 을 } \\ & \text { 응 } \end{aligned}$ | $\begin{aligned} & \text { İ } \\ & \text { U } \\ & \frac{0}{0} \\ & \text { E } \\ & \hline \end{aligned}$ | 0 <br> 1 <br> 0 <br> 0 | $\begin{aligned} & \frac{\varepsilon}{\bar{C}} \\ & \frac{\bar{\omega}}{\Phi} \end{aligned}$ | $\begin{aligned} & \infty \\ & 0 \\ & 0 \\ & 0 \\ & 4 \\ & \hline 0 \\ & \frac{\varepsilon}{\omega} \end{aligned}$ |  |  | $\begin{aligned} & \frac{\cong}{\overline{0}} \\ & \frac{0}{0} \\ & \frac{0}{0} \end{aligned}$ |  | $\begin{aligned} & \text { © } \\ & \text { O4 } \\ & \text { 을 } \\ & \text { 읃 } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Largemouth Bass | 19 | 5 | 361 | 0.6 | 350 | 79 | 450 | 6.1 | 39 | 1.0 | ND | ND | ND |
| White Catfish | 11 | 5 | 258 | 0.8 | 280 | 15 | 180 | 20 | 130 | 5 | ND | ND | ND |
| Black Bullhead | 3 | 4-5 | 288 | 0.6 | 140 | 49 | 140 | 3.2 | 15 | ND | ND | ND | ND |
| Corbicula | 2-3 | 24-68 | 31 | 1.4 | 12 | 1000 | 310 | 64 | 48 | 7.5 | 2.7 | ND | 2.9 |

Canal to a high of $470 \mathrm{ng} / \mathrm{g}$ at San Joaquin River at Bowman Road. Four of eleven locations had concentrations in white catfish that exceeded the screening value (Table 2, Figure 4). Similar to the largemouth bass, many locations in the central and southern Delta were below the screening value. White catfish were only found at one location upstream on the San Joaquin River (at Landers Avenue) where a concentration of $250 \mathrm{ng} / \mathrm{g}$ was observed. Mercury concentrations in white catfish at seven SRWP locations in 1997 were all above the screening value (Figure 4).

The median concentration for three black bullhead samples was much lower (141

Figure 2. Mercury concentrations in Delta fish and Corbicula, and Sacramento River watershed fish, 1998.


Table 2. Summary of concentrations above screening values for each species. Numerator indicates the number above the screening value, denominator indicates the number of samples analyzed. Composite samples only. All units $n g / g$ wet weight.

| Species |  |  |  |  |  |  |  | ᄃ - - - ¢ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| screening value | 300 | 1000 | 20000 | 20* | 100 | 30 | 2 | 300 | 10000 |
| Largemouth Bass | 11/19 | 0/19 | 0/19 | 3/19 | 1/19 | 0/19 | 0/19 | 0/19 | 0/19 |
| White Catfish | 4/11 | 0/11 | 0/11 | 6/11 | 6/11 | 0/11 | 1/11 | 0/11 | 0/11 |
| Black Bullhead | 0/3 | 0/3 | 0/3 | 0/3 | 0/3 | 0/3 | 0/3 | 0/3 | 0/3 |
| Corbicula | 0/3 | 2/3 | 0/3 | 1/2 | 0/2 | 0/2 | 1/2 | 0/2 | 0/2 |
| All species | 15/36 | 2/36 | 0/36 | 10/35 | 7/35 | 0/35 | 2/35 | 0/35 | 0/35 |

* screening value is for sum of Aroclors; data are sum of congeners
$\mathrm{ng} / \mathrm{g}$ ) (Table 1). All of these were below the screening value (Table 2). Mercury concentrations in Corbicula were much lower than in the fish, with a median of 12 $\mathrm{ng} / \mathrm{g}$ in three samples (Table 1).


## Controlling Factors

Within a given species, the older and larger fish tend to have higher mercury concentrations. At two locations, Port of Stockton and Sycamore Slough, largemouth

Figure 3. Mercury concentrations in largemouth bass at each sampling location. Data from this study and the SRWP (see figure 1).


Figure 4. Mercury concentrations in white catfish at each sampling location. Data from this study and the SRWP (see figure 1).

bass were caught that exceeded the size range set for composite samples. Largemouth bass were analyzed individually at these locations to take advantage of the wider size range available for inclusion in regressions of mercury with size or age. Individual largemouth bass were also analyzed at the San Joaquin River at Vernalis, where enough fish were collected to prepare duplicate composite samples (i.e., 10 largemouth bass).

In spite of small samples sizes and the limited size range sampled, some significant regressions (three of six) were obtained for both age and length versus mercury concentration (Figures $5 \mathrm{a}, \mathrm{b}$ ). The fit of the linear regressions were similar for both length and age, although perhaps slightly better overall for length. The inclusion of the large fish ( $>438 \mathrm{~mm}$ ) caught at Port of Stockton and Sycamore Slough helped reveal the relationships with age and length. Regressions for length versus mercury at these two locations were both significant. At San Joaquin River at Vernalis a larger number of fish were available for analysis, but the fish were all in the target size range $(305-438 \mathrm{~mm})$ for composite samples. These individual data indicate confirm that length and age are important variables influencing mercury concentrations in Delta largemouth bass. The limited size ranges selected in this study facilitate comparability of the composite samples, but constrain the ability to assess relationships between size and mercury concentration. Evaluation of broader size ranges in the future would yield information that would be valuable in assessment of human health risks.

Figure 5. a) Mercury concentration versus age in individual largemouth bass: 1) San Joaquin River at Vernalis; 2) Port of Stockton; 3) Sycamore Slough. b) Mercury concentration versus length in individual largemouth bass: 1) San Joaquin River at Vernalis; 2) Port of Stockton; 3) Sycamore Slough.



## Spatial Patterns

Substantial regional variation was observed in mercury concentrations in largemouth bass. Largemouth bass from the Delta (from Vernalis downstream in the south and downstream of SRWP sites in the north) had an average mercury concentration in composite samples of $290 \mathrm{ng} / \mathrm{g}$. The average mercury concentration measured in the SRWP for largemouth bass in the lower Sacramento River and northern Delta was $650 \mathrm{ng} / \mathrm{g}$, more than twice as high as the Delta average. The average concentration in San Joaquin River (upstream of Vernalis) largemouth bass ( $490 \mathrm{ng} /$ g) was also elevated relative to the Delta. Many of the samples analyzed in the Delta had concentrations below the $300 \mathrm{ng} / \mathrm{g}$ screening value, while all but one sample from the SRWP region and all samples from the San Joaquin region were above the screening value (Figure 3).

Given the clear relationship with length observed at the locations where individual largemouth bass were analyzed, accounting for variation in age or length when comparing locations yields a clearer picture of spatial variation. Plots of mercury concentration versus length allow visual comparisons that incorporate size differences (Figures 6 and 7).

On the largemouth bass plot (Figure 6), the regression lines obtained from

Figure 6. Mercury concentrations versus average fish length in composite samples of largemouth bass. Data from this study and the SRWP (see figure 1).

individual fish at the three locations are provided for reference. Several SRWP locations (Feather River at Nicolaus, Sacramento River at Alamar, Sacramento River at River Mile 44, and Cache Slough near Ryer Island Ferry) had high concentrations relative to length. Several stations from the central and southern Delta (Port of Stockton, Smith Canal, San Joaquin River at Turner Cut, White Slough, San Joaquin River near Potato Slough, San Joaquin River at Point Antioch, Middle River at

Figure 7. Mercury concentrations versus average fish length in composite samples of white catfish. Data from this study and the SRWP (see figure 1).


Bullfrog, and Old River near Paradise Cut) had relatively low concentrations relative to length. The central and southern Delta appears to have some peculiar characteristics that result in low mercury bioaccumulation at higher trophic levels.

The white catfish plot shows similar regional variation (Figure 7). Several central and southern Delta locations (Smith Canal, San Joaquin River at Turner Cut, Port of Stockton, and Middle River at Bullfrog) had low concentrations relative to length. As in largemouth bass, the SRWP site at Sacramento River at Alamar had a high concentration. The lack of information on the typical slope of the length-mercury regression line makes it difficult to evaluate the magnitude of concentrations relative to length for the other locations.

Even taking into account size differences, concentrations in largemouth bass composites still exhibited substantial spatial variation, with up to an 8 -fold difference between locations in equal-sized fish (Smith Canal-84 ng/g vs. Cache Slough-660 $\mathrm{ng} / \mathrm{g}$ ). Factors other than length must be responsible for this remaining variation. These factors are influential enough to cause observed concentrations to vary from well below the screening value to well above the screening value. Mercury concentrations in white catfish were also influenced by factors other than length or age that resulted in samples being either well below or well above the screening value. Possible explanations for the spatial variation observed in these species include spatial variation in total mercury concentrations, mercury methylation and bioavailability, or trophic position. Research funded by CalFED on mercury cycling in the Delta will help determine the relative importance of these other factors.

## Temporal Trends

Mercury data from TSMP sampling in the Delta can be compared to the results of this study and the SRWP to provide a limited indication of trends over the last two decades. This is only a limited indication because TSMP sampling in the Delta was generally limited and sporadic.

The best historical time series were generated by the TSMP for white catfish at the Sacramento River at Hood and the San Joaquin River at Vernalis, and sampling at these locations has been continued by the SRWP and the Delta Study to further extend the series (Figures 8a and b). Data for white catfish suggest that concentrations have declined from the late 1970s to the mid-1980s and remained relatively constant from the mid-1980s to 1998. At the Sacramento River at Hood/RM 44 the time series suggests

Figure 8. Mercury concentration versus length in white catfish: a) Sacramento River at Hood/RM44; b) San Joaquin River at Vernalis. Data from this study, TSMP, and SRWP.


Composite White Catfish San Joaquin River at Vernalis

that concentrations have declined since the late 1970s (Figure 8a). The mercurylength plot shows that concentrations in 1978-1983 were high relative to length (i.e., they have relatively large positive residuals from the regression line). The most recent results from 1997 and 1998 (duplicate samples were collected in both years) fall near or below the regression line; two of the four 1997 and 1998 samples were below the screening value.

The mercury-length plot for the San Joaquin River at Vernalis shows that concentrations in white catfish in 1998 were low relative to previous measurements (Figure $8 \mathrm{~b})$. The time series for this location is not as complete as for the Sacramento River at

Hood. One point (from 1986)

Figure 9. Mercury concentration versus length in largemouth bass at Sacramento River at Hood/RM44 and San Joaquin River at Vernalis. Data from this study, TSMP, and SRWP.

representing two very large fish appears to be an outlier and is not included in the graph. Both of the 1998 samples were above the screening value.

The data for largemouth bass are less complete and only go back to the late 1980s (Figure 9). Two composite samples collected in 1998 at Sacramento River at Hood/RM44 of similar size had very similar mercury concentrations (both were $710 \mathrm{ng} / \mathrm{g}$ ). A 1988 composite sample of similar size had only $390 \mathrm{ng} / \mathrm{g}$ mercury. Although the recent data are higher than historic data for fish of similar size, the small number of samples provide an insufficient basis for discussion of long term trends.

## PCBs

## Introduction

The term "polychlorinated biphenyl" refers to a group of 209 individual chemicals ("congeners")
based on substitution of the biphenyl molecule with varying numbers of chlorine atoms. Due to their resistance to electrical, thermal, and chemical processes, PCBs were used in a wide variety of applications (e.g., in electrical transformers and capacitors, vacuum pumps, hydraulic fluids, lubricants, inks, and as a plasticizer) from the time of their initial commercial production in 1929 (Brinkmann and de Kok, 1980). In the U.S., PCBs were sold as mixtures of congeners known as "Aroclors" with varying degrees of chlorine content. By the 1970s a growing appreciation of the toxicity of PCBs led to restrictions on their production and use. In 1979, a final PCB ban was implemented by the U.S. Environmental Protection Agency, prohibiting the manufacture, processing, commercial distribution, and use of PCBs except in totally enclosed applications. A significant amount of PCBs remains in use in these applications: a recent voluntary survey in the Bay Area found that approximately 200,000 kg
of PCBs are currently in use in transformers. Leakage from or improper handling of such equipment has led to PCB contamination of runoff from industrial areas. Other sources of PCBs to the Estuary are atmospheric deposition, effluents, and remobilization from sediment (Davis et al. 2000).

In spite of the fact that their use has been restricted for almost two decades, PCBs remain among the environmental contaminants of greatest concern because many of the PCB congeners are potent toxicants that are resistant to degradation and have a strong tendency to accumulate in biota. In general, PCBs are not very toxic in acute exposures, but certain congeners are extremely toxic in chronic exposures. The most toxic PCB congeners are those that closely mimic the potency and mechanism of toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin ("dioxin," one of the most toxic compounds known). These PCB congeners can cause toxic symptoms similar to those caused by dioxin exposure, including developmental abnormalities and growth suppression, disruption of the endocrine system, impairment of immune function, and cancer promotion (Ahlborg et al., 1994). Other toxicologically active PCB congeners and their metabolites exert toxicities through different mechanisms than the dioxin-like congeners (McFarland and Clarke, 1989). U.S. EPA classifies PCBs as a probable human carcinogen (U.S. EPA, 1995).

The toxicity of PCBs has historically been evaluated for Aroclor mixtures. In recent years toxicological data have begun to accumulate for specific PCB congeners, but overall the toxicological database is more complete for Aroclor mixtures than for PCB congeners (U.S. EPA 1995). U.S. EPA (1995) consequently recommends using an Aroclor screening value to evaluate fish tissue contamination. In this study PCBs were measured on a congener-specific basis. Advantages of congener-specific data are described in Davis et al. (1997) and U.S. EPA (1995). The congener-specific results were used to estimate Aroclor concentrations.

Due to their general resistance to metabolism and high affinity for lipids, PCBs and other similar organochlorines reach higher concentrations with increasing trophic level in aquatic environments; this process is known as "biomagnification" (Gobas et al., 1993, Suedel et al., 1994). The dioxin-like PCB congeners are also relatively resistant to metabolism (Davis 1997). Consequently, predatory fish, birds, and mammals (including humans that consume fish) at the top of the food web are particularly vulnerable to the effects of PCB contamination.

## Analytical considerations

PCBs were measured on a congener-specific basis. A list of 48 congeners was selected for analysis, based on abundance in fish and other media in the Estuary (SFEI 2000) and including specific congeners that are useful indicators of distinct Aroclor mixtures (Newman et al. 1998). Some PCBs have dioxin-like potency, including several congeners measured in this study. Most of the dioxin equivalents due to PCBs in fish are attributable to congeners not measured in this study, especially PCB 126 (SFEI 1999). PCB dioxin-equivalents are therefore not presented in this report.

Screening values for PCBs are expressed as Aroclors. Previous work in the Bay (SFBRWQCB 1995, SFEI 1999) has shown that PCB concentrations expressed as the sum of PCB congeners are slightly lower than those expressed as sums of Aro-
clors. In this report sums of congeners are compared to the Aroclor-based screening value. It should be noted that if the data were expressed as sums of Aroclors it is possible that more samples would exceed the screening value.

A sum of PCB congeners could be quantified in each sample. The reporting limit for each congener was $0.20 \mathrm{ng} / \mathrm{g}$ wet. In the lowest sample, only one congener was quantified and the sum of congeners was only $0.23 \mathrm{ng} / \mathrm{g}$. Concentrations near reporting limits have relatively high uncertainty associated with them and should be considered as only semi-quantitative.

## Data distribution and summary statistics

Of the three fish species sampled, white catfish had the highest median PCB concentration ( $20 \mathrm{ng} / \mathrm{g}$ ) (Table 1, Figure 10). PCB concentrations in white catfish ranged from a low of $8 \mathrm{ng} / \mathrm{g}$ at Middle River at Bullfrog to a high of $102 \mathrm{ng} / \mathrm{g}$ at Smith Canal. Six of eleven locations had concentrations above the $20 \mathrm{ng} / \mathrm{g}$ screening value (Table 2, Figure 11). Locations above the screening value were scattered around the Delta. In the SRWP, PCB concentrations in white catfish at two of four locations in 1997 were above the screening value (Figure 11).

The median PCB concentration in largemouth bass was $6 \mathrm{ng} / \mathrm{g}$ (Table 1), with a range from $2 \mathrm{ng} / \mathrm{g}$ at Mokelumne River to a high of $112 \mathrm{ng} / \mathrm{g}$ at Smith Canal. Three of 19 locations where largemouth bass were collected had concentrations above the screening value (Table 2). Two of these were in the Stockton area (Smith Canal and

Figure 10. PCB concentrations in Delta fish and Corbicula, and Sacramento River watershed fish, 1998.


Figure 11. PCB concentrations in white catfish at each sampling location. Data from this study and the SRWP (see figure 1).


Figure 12. PCB concentrations in largemouth bass at each sampling location. Data from this study and the SRWP (see figure 1).


Port of Stockton). The third was at the Stanislaus River location. One of the SRWP locations (Sacramento River at RM44) exceeded the screening value (Figure 12). PCB concentrations in the largemouth bass analyzed individually ranged from 0.2 $\mathrm{ng} / \mathrm{g}$ (San Joaquin River at Vernalis) to $46 \mathrm{ng} / \mathrm{g}$ (Port of Stockton).

None of the black bullhead composites exceeded the screening value.
Two Corbicula composite samples, from the Port of Stockton and Sacramento River at Rio Vista, were analyzed for organics. The sample from the Port of Stockton had an unusually high concentration of PCBs ( $112 \mathrm{ng} / \mathrm{g}$ wet). Expressed on a dry weight basis (for comparison with other Corbicula datasets) this sample had $870 \mathrm{ng} / \mathrm{g}$ of PCBs. This concentration is higher than any concentration observed in Corbicula in RMP sampling, and compares to the highest concentrations observed for any bivalve species in RMP sampling (SFEI 2000). The wet weight concentration was well above the screening value. The sample from Rio Vista had a much lower concentration ( $16 \mathrm{ng} / \mathrm{g}$ wet, $160 \mathrm{ng} / \mathrm{g}$ dry).

## Controlling factors

PCBs accumulate in lipid, and, other factors being equal, fish fillets with higher lipid content are expected to contain higher PCB concentrations. The analysis of organics in individual largemouth bass at three locations provided an opportunity to examine variation among individuals and correlations with lipid at single locations (Figure 13). PCB 138 was detected in every sample and was the best quantified PCB congener; this congener was used in the regressions to avoid the noise that would be introduced by the influence of non-quantitative (below reporting limit) results on sums of PCBs. A highly significant regression was obtained for Sycamore Slough ( $\mathrm{R}^{2}=0.89, \mathrm{p}=0.0004$ ). San Joaquin River at Vernalis also yielded a significant result ( $\mathrm{R}^{2}=0.50, \mathrm{p}=0.02$ ). The regression for Port of Stockton was not significant, however this appears to be due to two fish with unusually high concentrations. These fish may have foraged in a relatively contaminated area. Overall, the individual largemouth bass data indicate that lipid content is an important variable influencing PCB concentrations in Delta largemouth bass. Small scale spatial variation in concentrations may also play a role in

Figure 13. PCB 138 concentrations versus lipid in largemouth bass at three locations.


Port of Stockton


Sycamore Slough

contaminated areas like the Port of Stockton.

## Spatial Patterns

Data from this study, along with data from the SRWP and TSMP, suggest the presence of localized PCB hotspots with concentrations of concern in the Central Valley, rather than broad regional patterns such as were seen for mercury. The locations with relatively high concentrations included Smith Canal ( $102 \mathrm{ng} / \mathrm{g}$ in white catfish and $112 \mathrm{ng} / \mathrm{g}$ in largemouth bass), Sacramento River at RM 44 (largemouth bass up to $117 \mathrm{ng} / \mathrm{g}$ and white catfish up to $57 \mathrm{ng} / \mathrm{g}$ ), American River at Discovery Park ( $59 \mathrm{ng} / \mathrm{g}$ in white catfish), Port of Stockton ( $51 \mathrm{ng} / \mathrm{g}$ in white catfish and $27 \mathrm{ng} /$ g in largemouth bass), San Joaquin River at Vernalis (up to $38 \mathrm{ng} / \mathrm{g}$ in white catfish), and San Joaquin River at Bowman Road ( $36 \mathrm{ng} / \mathrm{g}$ in white catfish). The Corbicula sample from the Port of Stockton also indicated relatively high PCB concentrations at that location.

Given the relationship between trace organic accumulation and lipid content, accounting for variation in lipid yields a clearer picture of spatial or temporal variation. Plots of PCB concentration versus lipid content (Figures 14 a and b ) allow visual comparisons that factor out differences related to varying lipid content. In white catfish (Figure 14a), samples from Smith Canal, American River at Discovery Park, Port of Stockton, and San Joaquin River at Bowman Road had relatively high concentrations in spite of their low lipid content, suggesting relatively high rates of PCB accumulation. White catfish from San Joaquin River at Vernalis and Sacramento River at RM44 reached relatively high concentrations (greater than $35 \mathrm{ng} / \mathrm{g}$ ), but this appears to be attributable to the high lipid content of these samples. In largemouth bass (Figure 14b), samples from Smith Canal and Sacramento River at RM44 stood out with much higher concentrations than other largemouth samples with similar lipid content. The congener profile of the Sacramento River at RM44 sample was very unusual; results of further sampling will help determine whether this result is truly indicative of persistent PCB contamination at this location. Largemouth bass from the Port of Stockton were also somewhat elevated relative to other largemouth samples with similar lipid content.

PCB congener profiles, or "fingerprints," also provide information on spatial variation. Spatial variation in PCB fingerprints is evidence of spatial variation in PCB sources. The white catfish and largemouth bass samples from Smith Canal both were elevated in congeners 149, 180, 187, and other congeners indicative of Aroclor 1260. The Corbicula composite from the Port of Stockton was high in congeners 28, 44, 49, and 52, which are indicative of Aroclor 1248, and also in congeners 95, 101, 110, and 118, which are indicative of Aroclor 1254. Several largemouth bass from the Port also had relatively high proportions of Aroclor 1248 and 1254 congeners. Other largemouth from the Port lacked these distinct profiles. This variation in PCB fingerprints at the Port is probably indicative of small scale variation in contamination of foraging areas. Another distinct fingerprint was observed for the largemouth bass sample from Stanislaus River, which had relatively high proportions of congeners 201, 203, 206, and 209, which are indicative of the most highly chlorinated Aroclors (Aroclor 1262 or higher).

Some of the locations identified as having persistent PCB contamination in the

Delta Study and SRWP sampling also had high concentrations in TSMP sampling. High PCB concentrations at the Sacramento River at Hood have been observed in white catfish (up to 198 ppb in 1983 and 124 ppb as recently as 1992) and carp (up to 480 ppb in 1985). Past sampling also found high concentrations in the south Delta, including the Stockton Deep Water Channel (240 ppb in white catfish in 1986 and 100 ppb in largemouth bass in 1990), the San Joaquin River at Vernalis (up to 282 ppb , the statewide maximum, in white catfish in 1986 and up to 314 ppb in channel catfish in 1984), Old River, and Paradise Cut near Tracy. Other locations in the watershed with high PCB concentrations in past sampling include the Feather River downstream of Highway 99, Beach Lake, Natomas East Main Drain, the Stanislaus River, and the Tuolumne River at the San Joaquin River.

Overall, the available data indicate that PCB contamination has been widespread in the Central Valley, and that significant contamination remains in some locations, including the Sacramento River in the north Delta, and the Port of Stockton, Smith Canal, and other locations in the south Delta. Available information on historic uses of PCBs suggest the likelihood that significant localized PCB contamination also exists in other areas not covered in the SRWP and Delta Study.

Figure 14. PCB concentrations (sum of congeners) versus percent lipid in composite samples: a) white catfish; b) largemouth bass.


## Temporal trends

The limited data available for evaluating long term trends suggest that PCB concentrations have declined in the Delta, although the apparent drop is not as distinct as that observed for the OC pesticides and some samples still exceed the PCB screening value. In addition to the paucity of data points, the use of different and relatively insensitive analytical methods in the older TSMP obscures the long term record.

The best historical time series were generated by the TSMP for white catfish at the Sacramento River at Hood and the San Joaquin River at Vernalis, and sampling at these locations has been continued by the SRWP and the Delta Study to further extend the series (Figures

Figure 15. PCB concentrations ( $\mathrm{ng} / \mathrm{g}$ lipid) in white catfish from two locations. Data from this study, the SRWP, and the TSMP.



15 a and b ). Some of the highest concentrations recorded for white catfish in the TSMP were obtained at these two locations. At the Sacramento River at Hood, concentrations measured in 1997 and 1998 (ranging from 14 to $30 \mathrm{ng} / \mathrm{g}$ lipid as the sum of congeners) were at the low end of the range of concentrations recorded by the TSMP from 1980 to 1993 (18 to $168 \mathrm{ng} / \mathrm{g}$ lipid as the sum of Aroclors). At the San Joaquin River at Vernalis the 1998 results ( 30 and $33 \mathrm{ng} / \mathrm{g}$ lipid) are lower than the TSMP maximum for this location ( $109 \mathrm{ng} / \mathrm{g}$ lipid in 1987), but comparable to other historic values. Other values obtained for white catfish from other locations compare to the higher concentrations measured historically, especially the $102 \mathrm{ng} / \mathrm{g}$ wet ( $232 \mathrm{ng} / \mathrm{g}$ lipid) measured at Smith Canal and the $51 \mathrm{ng} /$ g wet ( $84 \mathrm{ng} / \mathrm{g}$ lipid) measured at the Port of Stockton. In largemouth bass, the historical TSMP data have too many below detection limit results for a useful comparison.


It should be noted that the recent data are not directly comparable with the older data from the TSMP. One reason for this is that the recent data (1997 and 1998) are sums of congeners, while the older data are Aroclor measurements. When expressed on an Aroclor basis, the recent data would be slightly higher than indicated by the sum of the congeners. Another reason that the data may not be comparable is the use of different methods for measuring lipids. From the late 1970s to 1998, the TSMP used a gravimetric method for lipid determination employing a petroleum ether extraction. The method employed in the recent studies is also gravimetric, but based on an accelerated solvent extraction in dichloromethane and acetone. The use of different lipid methods can introduce a 2 to 3 -fold difference in lipid data (Henry Lee, U.S. EPA, personal communication).

In summary, the limited long term trend data available suggest possible declines in PCB concentrations, but concentrations in a few locations remain high relative to historical results and above human health screening values. There are likely other locations not yet identified where elevated concentrations persist. The variability of the data and the use of an insensitive analytical method in the TSMP contribute to the difficulty in drawing firmer conclusions.

## Organochlorine Pesticides

Organochlorine (OC) pesticides (including DDT, chlordane, dieldrin, toxaphene, and others) were used in a wide variety of applications in agricultural, domestic, and industrial settings. Since these chemicals are so persistent, concentrations remain elevated in areas where they were used decades ago. Runoff from these areas continues to transport OC residues into creeks, rivers, and, ultimately, the Estuary.

The primary use of these chemicals was in agriculture. From the first widespread use of DDT in World War II to its cancellation in 1972, a total of approximately $1,350,000,000$ pounds was used in the U.S. (U.S. EPA 1975). In the 1960s DDT was used heavily on cotton, a crop which was particularly reliant on insecticides. Cotton accounted for $50 \%$ of all agricultural crop insecticide use in the 1960 s, and the approximately $20,000,000 \mathrm{lbs} / \mathrm{yr}$ of DDT used on cotton accounted for $30 \%$ of the total cotton insecticides (U.S. EPA 1975). This was $75 \%$ of the total DDT used on all crops. Areas of cotton production in the 1950s and 1960s in the Central Valley therefore are potential sites of historical contamination with both DDT. Limited data are available on DDT use in California. Pesticide use reporting began in 1970, when DDT use was waning rapidly. DDT use in 1970 was $1,165,000 \mathrm{lbs}$, dropping to $111,000 \mathrm{lbs}$ in 1971 and $81,000 \mathrm{lbs}$ in 1972. From 1973 on less than 200 lbs per year were used (Mischke et al. 1985). A 1984 statewide survey of DDT concentrations in soils from agricultural areas found DDT residues wherever DDT was used historically, and concluded that residues from legal agricultural applications of DDT appeared to be the source of continuing DDT contamination in California rivers at that time (Mischke et al. 1985). This conclusion is probably still true today.

Dieldrin is another OC pesticide that still is sometimes found at concentrations of potential concern in fish tissue in the Central Valley. In addition to being used in agriculture, dieldrin was used extensively for structural termite control. Dieldrin was used on more than 40 agricultural crops and for soil treatment around various fruits,
nuts, and vegetables, and also in mosquito control, as a wood preservative, and in moth proofing (Harte et al. 1991, U.S. EPA 1995). All uses on food products were suspended in 1974. All uses except subsurface termite control, dipping of nonfood roots and tops, and moth proofing in a closed system were banned in 1985. These remaining uses were voluntarily canceled by industry. Due to its widespread use in termite control in addition to agricultural pest control, dieldrin residues are found in both urban and agricultural areas.

In spite of the fact that the use of OC pesticides has been restricted for decades, these chemicals remain environmental contaminants of concern because of their persistence in the environment, their strong tendency to accumulate in biota, and their toxicity. The carcinogenicity of OC insecticides is the toxic effect of greatest concern from a regulatory perspective. DDT and dieldrin are considered probable human carcinogens (U.S. EPA 1995). In San Francisco Bay, the cancer risk associated with the concentrations of DDT, dieldrin, and chlordane in fish is responsible for the inclusion of these chemicals in the current fish consumption advisory (OEHHA 1994). Inclusion of these chemicals in the fish consumption advisory has subsequently resulted in these chemicals being targeted as priorities for regulatory action by the Regional Water Quality Control Board and U.S. EPA.

Endocrine disruption is another human health concern associated with OC insecticides. Many OC pesticides, including DDT and dieldrin, have endocrine activity. Endocrine disruption is also a concern in wildlife exposed to OC pesticides. In particular, piscivorous birds and mammals have much higher OC exposure than humans and face greater risks. Effects of OC pesticides on development and survival of early life stages are a particular concern in wildlife.

Although other OC pesticides were also analyzed (see Appendix A), only DDT and dieldrin had concentrations above screening values. The following discussion therefore focuses on these two contaminants. Other OC pesticides are briefly discussed in a subsequent section.

## Analytical considerations

Seven DDT compounds (isomers and metabolites) were analyzed. Following U.S. EPA (1995) guidance, six DDT compounds were summed to derive "sum of DDTs": p,p'-DDT, o, p'-DDT, p,p'-DDE, o, p'-DDE, p,p'-DDD, and o,p’-DDD. The screening value for DDTs, $100 \mathrm{ng} / \mathrm{g}$, applies to the sum of DDTs. Detectable DDT compounds were present in all of the 47 samples analyzed. p,p-DDE was the most abundant compound and the only one present in every sample. The reporting limits for individual DDT compounds ranged between 2 and $5 \mathrm{ng} / \mathrm{g}$.

Dieldrin was present above the reporting limit ( $2 \mathrm{ng} / \mathrm{g}$ ) in only 3 of 47 samples analyzed.

## Data distribution and summary statistics

White catfish had the highest median DDT concentration (138 ng/g) of the three fish species sampled (Table 1, Figure 16). DDT concentrations in white catfish ranged from a low of $42 \mathrm{ng} / \mathrm{g}$ at Smith Canal to a high of $407 \mathrm{ng} / \mathrm{g}$ at San Joaquin River at Bowman Road. Six of eleven locations had concentrations above the $100 \mathrm{ng} /$
g screening value (Table 2). Locations above the screening value were concentrated in the south Delta (Figure 17).

The median DDT concentration in largemouth bass was $39 \mathrm{ng} / \mathrm{g}$ (Table 1, Figure 16), and ranged from a minimum of $6 \mathrm{ng} / \mathrm{g}$ at Sycamore Slough to a maximum of $113 \mathrm{ng} / \mathrm{g}$ at Stanislaus River. Only one of nineteen samples (at Stanislaus River) exceeded the $100 \mathrm{ng} / \mathrm{g}$ screening value (Table 2, Figure 18).

None of the black bullhead samples approached the $100 \mathrm{ng} / \mathrm{g}$ screening value.

DDT concentrations in the two Corbicula samples were $77 \mathrm{ng} /$ g wet ( $590 \mathrm{ng} / \mathrm{g}$ dry) at Port of Stockton and $19 \mathrm{ng} / \mathrm{g}$ wet ( 180 $\mathrm{ng} / \mathrm{g}$ dry) at Sacramento River at Rio Vista. These Port of Stockton concentration is higher than the concentrations measured in clams at RMP stations in the western Delta (SFEI 2000), but lower than concentrations measured further upstream in the San Joaquin River watershed (Pereira et al. 1996, Brown 1998). Concentrations of DDT in Corbicula as high as 4300 $\mathrm{ng} / \mathrm{g}$ dry have been reported from Orestimba Creek in the western San Joaquin Valley (Pereira et al.

Figure 16. DDT concentrations in Delta fish and Corbicula, and Sacramento River watershed fish, 1998.
 1996). Neither of the two Corbicula samples exceeded the DDT screening value.

Dieldrin was detected in only 3 of 47 samples. The reporting limit for dieldrin was the same as the screening value ( $2 \mathrm{ng} / \mathrm{g}$ ), so all three samples with detectable dieldrin were above the screening value (Table 2). A white catfish composite from San Joaquin River at Landers Avenue had $2.9 \mathrm{ng} / \mathrm{g}$ (Figure 19). An individual largemouth bass from Sycamore Slough had $2.3 \mathrm{ng} / \mathrm{g}$ (Figure 20). None of the other individual largemouth bass from Sycamore Slough had detectable dieldrin. A Corbicula composite from Port of Stockton had $5.4 \mathrm{ng} / \mathrm{g}$ wet weight ( $42 \mathrm{ng} / \mathrm{g}$ dry weight), a relatively high concentration compared to concentrations for Corbicula reported in other studies (Pereira et al. 1996, Brown 1998, SFEI 2000). The highest concentration observed in the USGS studies was in the San Joaquin Valley (Pereira et al. 1996, Brown 1998) was $9.8 \mathrm{ng} / \mathrm{g}$ wet in Orestimba Creek. In the SRWP six samples have exceeded the dieldrin screening value: three largemouth bass (Figure 20), one white catfish (Figure 19), one Sacramento pike minnow, and one carp.

Figure 17. DDT concentrations in white catfish at each sampling location. Data from this study and the SRWP (see figure 1).


Figure 18. DDT concentrations in largemouth bass at each sampling location. Data from this study and the SRWP (see figure 1).


Figure 19. Dieldrin concentrations in white catfish at each sampling location. Data from this study and the SRWP (see figure 1).


Figure 20. Dieldrin concentrations in largemouth bass at each sampling location. Data from this study and the SRWP (see figure 1).


## Controlling Factors

Like PCBs, DDT accumulates in lipid, and fish fillets with higher lipid content are expected to contain higher concentrations. The analysis of organics in individual largemouth bass at three locations afforded an opportunity to examine correlations of lipid and DDT at single locations (Figure 21). In spite of the small number of samples available for each location, highly significant regressions were obtained at two of the three locations: Sycamore Slough $\left(\mathrm{R}^{2}=0.80, \mathrm{p}=0.003\right)$ and San Joaquin River at Vernalis $\left(\mathrm{R}^{2}=0.59, \mathrm{p}=0.009\right)$. The relationship at Port of Stockton was not statistically significant $\left(\mathrm{R}^{2}=0.20, \mathrm{p}=0.26\right)$. Overall, these data confirm that lipid content is an important variable influencing DDT concentrations in Delta largemouth bass.

## Spatial Patterns

Data from this study are consistent with past sampling indicating that the lower San Joaquin Valley watershed is a focal point for OC pesticide contamination. In

Figure 21. DDT concentrations versus lipid in largemouth bass at three locations.


Port of Stockton


Sycamore Slough
 white catfish, two south Delta locations had unusually high DDT concentrations: San Joaquin River at Vernalis ( 389 ppb ) and San Joaquin River at Bowman Road ( 407 ppb ). Several other white catfish samples from the south Delta were also above the screening value (Figure 17).

Given the relationship between DDT accumulation and lipid content, accounting for variation in lipid yields a clearer picture of spatial or temporal variation. Plots of DDT concentration versus lipid content (Figures 22 a,b) allow comparison of samples with similar lipid content. In white catfish a contiguous group of south Delta locations exhibited distinctly elevated DDT concentrations compared to other samples with similar lipid content (San Joaquin River at Bowman Road, San Joaquin River at Vernalis, San Joaquin River north of Highway 4, the Port of Stockton, Paradise Cut, and Old River), with the highest concentration at San Joaquin River at Bowman Road (Figure 22a). In largemouth bass, this same cluster of locations stands out with high concentrations relative to lipid content (Figure 22b).

The TSMP also found persistently high concentrations of OC pesticides in the south Delta. Common carp, channel catfish, and largemouth bass have been sampled frequently in the TSMP. White catfish have been sampled less frequently. High DDT concentrations in
carp have been observed in the south Delta at Paradise Cut (up to 5332 ppb in 1986) and the San Joaquin River at Vernalis (up to 1268 ppb in 1978). In channel catfish, some of the highest concentrations measured in California were obtained at the San Joaquin River at Vernalis, with concentrations over 2000 ppb in $1979,1984,1986$, and 1987. Channel catfish from the Stanislaus River ( 4149 ppb in 1990) and the Tuolumne River near the San Joaquin River ( 2570 ppb in 1979) have also had very high DDT concentrations. In white catfish, the highest values measured in California have been from the San Joaquin River at Vernalis, with a maximum of 2220 ppb in 1987. The south Delta is clearly influenced by historic DDT use and environmental contamination.

The highest dieldrin concentrations in the watershed have also been measured in the south Delta. Several channel catfish samples from the San Joaquin River at Vernalis have had high concentrations, with a maximum of 44 ppb in 1984. White catfish from the San Joaquin River at Vernalis have had several of the highest dieldrin concentrations in the State, including the statewide maximum for white catfish of 53 ppb . Carp from another south Delta location, Paradise Cut near Tracy, also had some of the highest dieldrin concentrations in the State, including measurements of 60 ppb in 1986 and 37 ppb in 1989. Other high dieldrin concentrations have been recorded in samples from the north Delta, including carp and white catfish from the Sacramento River at Hood, and channel catfish from the Colusa Basin Drain.

Overall, the results of this study are consistent with historic data from the TSMP, indicating that the south Delta is an area with particularly high OC pesticide concentrations. Studies by USGS have also found high concentrations of OC pesticides in sediment and biota in the lower San Joaquin River watershed (Pereira et al. 1996,


Brown 1998) and documented transport of contaminated sediments from this region to the San Joaquin River (Kratzer 1998).

## Temporal trends

In general, OC pesticide concentrations in the Central Valley have declined considerably since the late 1970s and early 1980s. Most concentrations in the recent samples are lower than those measured in the TSMP. Relatively good time series were generated by the TSMP for white catfish at the Sacramento River at Hood and the San Joaquin River at Vernalis, and sampling at these locations has been continued by the Delta Study and SRWP to further extend the series. At the San Joaquin River at Vernalis, the 1998 DDT results are lower than the maximum concentration measured in 1988, but are comparable to several other concentrations measured in the early and mid-1980s (Figure 23a). At the Sacramento River at Hood, where concentrations have been historically lower than those at the San Joaquin River at Vernalis, recent SRWP results suggest a distinct decline ( $\mathrm{R}^{2}=0.50, \mathrm{p}=0.003$ ) from those measured in the early and mid-1980s (Figure 23b). These two time series suggest that the rate of decline varies among locations. It should be noted that due to the use of different methods of lipid determination, the recent data may not be directly comparable to the older TSMP data.

High concentrations observed in recent sampling also suggest that the rate of decline is slow at some locations. The 684 ppb of DDT in carp in the Colusa Basin Drain measured in the 1998 SRWP, for example, is higher than the concentrations in the Drain measured by the TSMP in the 1980s. Some of the more recent TSMP samples had relatively high concentrations, such as the 1990 channel catfish sample from the Stanislaus River ( 4149 ppb of DDT).

The most encouraging finding in the recent sampling is that chlordane was not above the 30 ppb screening value in any of the 1998 Delta Study or SRWP. The highest concentration of chlordane measured in this study was $16 \mathrm{ng} / \mathrm{g}$ in white catfish from San Joaquin River at Vernalis. Chlordane concentrations above 30 ppb had frequently been observed in the TSMP.

While OC pesticide contamination in Central Valley waterways is dissipating, some locations show a slow rate of decline. Significant concentrations persist in many locations, with some samples elevated well above screening values.

## Other Contaminants

This section provides brief discussions of the measured or potential exceedance of screening values of other contaminants measured in this study and of contaminants that were not measured in this study. Background information on the sources, chemistry, and toxicity of the chemicals in this section are provided in U.S. EPA (1995).

## Arsenic

The screening value for arsenic is $1000 \mathrm{ng} / \mathrm{g}$. This screening value applies to inorganic arsenic (U.S. EPA 1995). Organic arsenic, which comprises most of the arsenic in fish and shellfish tissue, is considered to be nontoxic. Total arsenic was

Figure 23. DDT concentrations (ng/g lipid) in white catfish from two locations. Data from this study, the SRWP, and the TSMP.

measured in this study. The maximum total arsenic concentration measured in fish was $180 \mathrm{ng} / \mathrm{g}$, indicating that inorganic arsenic in these samples must be far below the screening value. Two of three Corbicula samples had total arsenic concentrations above $1000 \mathrm{ng} / \mathrm{g}$. Inorganic arsenic in these samples was probably well below the screening value. If arsenic concentrations in Corbicula are spatially variable, it is possible that locations exist with higher concentrations than those measured in this study. Further sampling of Corbicula that includes analysis of inorganic arsenic is warranted.

## Selenium

The screening value for selenium is $20,000 \mathrm{ng} / \mathrm{g}$. Selenium was measured in this study, with a maximum concentration of $770 \mathrm{ng} / \mathrm{g}$ in largemouth bass from San Joaquin River at Vernalis, far below the screening value.

## Other organochlorine pesticides

Several other OC pesticides were measured in this study at concentrations below screening values, including chlordane, toxaphene, endosulfan, endrin, hexachlorobenzene, lindane (gamma-HCH), and mirex. Of these, toxaphene may have the greatest potential to be a human health concern. The screening value for toxaphene is $30 \mathrm{ng} / \mathrm{g}$, lower than the reporting limit of $50 \mathrm{ng} / \mathrm{g}$. No samples in this study were above $50 \mathrm{ng} / \mathrm{g}$. However, one sample in the SRWP in 1998 had detectable toxaphene (a carp composite from the Colusa Basin Drain with $120 \mathrm{ng} / \mathrm{g}$ ). It is possible that more samples above the screening value would have been detected in these studies if the reporting limit was $30 \mathrm{ng} / \mathrm{g}$ or lower. The highest concentration of chlordane ( $16 \mathrm{ng} / \mathrm{g}$ in white catfish at San Joaquin River at Vernalis) was well below the $30 \mathrm{ng} / \mathrm{g}$ screening value. Endosulfan, endrin, lindane, hexachlorobenzene, and mirex were not detected in any samples, and the reporting limits ( $5 \mathrm{ng} / \mathrm{g}, 2 \mathrm{ng} / \mathrm{g}, 1$ $\mathrm{ng} / \mathrm{g}, 0.3 \mathrm{ng} / \mathrm{g}$, and $3 \mathrm{ng} / \mathrm{g}$, respectively) were far below screening values ( $20,000 \mathrm{ng} /$ $\mathrm{g}, 1000 \mathrm{ng} / \mathrm{g}, 30 \mathrm{ng} / \mathrm{g}, 20 \mathrm{ng} / \mathrm{g}$, and $1000 \mathrm{ng} / \mathrm{g}$, respectively).

## Organophosphate pesticides

Two organophosphate (OP) pesticides were measured in this study: chlorpyrifos and diazinon. Diazinon, with a reporting limit of $20 \mathrm{ng} / \mathrm{g}$, was not detected in any sample. The screening value for diazinon is $300 \mathrm{ng} / \mathrm{g}$. Chlorpyrifos was detected in 11 of 47 samples analyzed. The maximum concentration was $7 \mathrm{ng} / \mathrm{g}$ in white catfish from San Joaquin River at Landers Avenue. This concentration was way below the screening value of $20,000 \mathrm{ng} / \mathrm{g}$.

## Polynuclear aromatic hydrocarbons (PAHs)

PAHs are efficiently metabolized by fish and do not accumulate in muscle tissue. Clams and other bivalves, on the other hand, do not readily metabolize PAHs, and PAHs do accumulate in these species. PAHs were measured in two clam composites. PAHs were only detected in the sample from Port of Stockton. A screening value exists for PAHs (U.S. EPA 1995) that is based on toxicology data for benzo(a)pyrene. U.S. EPA (1995) recommends that "benzo(a)pyrene equivalents" be calculated for seven PAHs. Doing this for the Port of Stockton sample yields a total of $0.02 \mathrm{ng} / \mathrm{g}$ of benzo(a)pyrene equivalent, well below the screening value of $3 \mathrm{ng} / \mathrm{g}$. The reporting limit for PAHs was $10 \mathrm{ng} / \mathrm{g}$. More extensive sampling with lower detection limits is needed to determine whether PAHs in Corbicula represent a potential human health concern.

## Other contaminants not measured in this study

Dioxins are a class of contaminants that were not measured in this study. Dioxins are probably present in the study area at concentrations above the $0.3 \mathrm{pg} / \mathrm{g}$ screening value for ITEQs. Dioxin analysis was not included in this study primarily because it is expensive to perform, and its inclusion would have significantly reduced the scope
of the sampling performed for other contaminants. In San Francisco Bay, limited dioxin analysis in 1994 (SFBRWQCB 1995) and in 1997 (SFEI 1999) found that every sample analyzed exceeded the screening value for ITEQs. Studies by CDHS (1997a,b) in the Port of Stockton also found that all samples analyzed (including largemouth bass, white catfish, carp, and bluegill) had concentrations above the ITEQ screening value. Based on these other findings, dioxins are probably present in the study area at concentrations above the $0.3 \mathrm{pg} / \mathrm{g}$ screening value for ITEQ.

Screening values also exist for the following compounds that were not analyzed in this study: cadmium, tributyltin, dicofol (an OC pesticide), disulfoton (OP pesticide), ethion (OP pesticide), terbufos (OP pesticide), and oxyfluorfen (chlorophenoxy herbicide). Data from the TSMP and OEHHA (1999) indicate that concentrations of cadmium, dicofol, and ethion are likely to be well below screening values. Data on concentrations of tributyltin, disulfoton, terbufos, and oxyfluorfen in fish tissue in California are not available.

## Summary and Conclusions

Of the chemicals measured in this study, the greatest concerns from a human health perspective are mercury, PCB , and DDT, which were frequently above screening values.

## Mercury

This study detected concentrations of mercury in sport fish that were frequently above the mercury screening value and generally similar to those for which consumption advice has been issued for the Bay. Half of the largemouth bass and white catfish samples analyzed in this study exceeded the mercury screening value (11 of 19 largemouth bass and 4 of 11 white catfish). Regional variation has been observed, with the highest concentrations in the lower Sacramento River watershed, moderately high concentrations in the lower San Joaquin River watershed, and generally low concentrations in the central Delta. Length and age are important variables influencing mercury concentrations, but other unidentified factors cause substantial additional variation. Other factors that may be causing the observed spatial variation include environmental concentrations of total mercury, mercury methylation, and trophic position. Concentrations appear to have declined from the late-1970s to the mid-1980s, but not from the mid-1980s to 1998. Studies of mercury in sport fish in the Delta and the Sacramento River are continuing with funding from CALFED and the Sacramento River Watershed Program. The objective of these studies is to provide the data needed to determine whether additional field studies or additional consumption advisories are needed for these regions.

## PCBs

Concentrations of PCBs were frequently above the PCB screening value. Thirty percent of the largemouth bass and white catfish samples were above the screening value ( 6 of 11 white cat and 3 of 19 largemouth). Data from this study and the SRWP suggest that PCBs are elevated in localized hotspots rather than on a regional
basis. Smith Canal particularly stood out in this study with high PCB concentrations in both white catfish and largemouth bass. The Port of Stockton also had relatively high PCB concentrations in the two fish species and in Corbicula. PCB congener profiles (or "fingerprints") indicated the presence of varying sources at different locations: Aroclor 1260 in Smith Canal, Aroclors 1248 and 1254 at Stockton, and Aroclor 1262 at Stanislaus River. Lipid was demonstrated to be an important variable influencing PCB concentrations. The limited long term trend data for the Delta suggest declines in PCB concentrations, but concentrations in a few locations remain high relative to historical results and above human health screening values.

## DDT

Concentrations of DDT exceeded the DDT screening value in $23 \%$ of the samples ( 6 of 11 white catfish and 1 of 19 largemouth bass). All of the samples above the screening value were obtained from the south Delta or lower San Joaquin River watershed. The results of this study are consistent with historic data from the TSMP and data from USGS studies indicating that the south Delta and lower San Joaquin River watershed are areas with particularly high OC pesticide concentrations. Lipid was demonstrated to be an important variable influencing DDT concentrations. In general, OC pesticide concentrations in the Central Valley have declined considerably since the late 1970s and early 1980s. Time series from two locations in the Delta suggest that the rate of decline varies among locations, with a slow rate of decline at some locations.

## Other Contaminants

Other chemicals which are possible concerns in the Delta include dieldrin, toxaphene, arsenic, PAHs, and dioxins. Dieldrin exceeded the screening value in one sample in this study. Data from this study were inconclusive for toxaphene, arsenic, and PAHs. Additional sampling with lower detection limits are needed to determine whether toxaphene concentrations in Delta fish exceed the screening value. Additional sampling of arsenic and PAHs in clams would be needed to determine whether screening values are exceeded in the region. Inorganic arsenic should be measured in future studies. Lower detection limits for PAHs should be employed to provide more definitive comparisons with screening values. Dioxins were not measured in this study due to a limited budget, but are likely to be above the screening value in Delta fish as they have been in previous studies in San Francisco Bay and the Port of Stockton. Data from this study indicate that the following contaminants do not represent a potential human health concern in the Delta: chlordane, selenium, endosulfan, endrin, hexachlorobenzene, lindane (gamma-HCH), mirex, diazinon, and chlorpyrifos.

## Overall Summary

Most of the samples analyzed exceeded at least one screening value. Of the 28 locations sampled in the Delta region in 1997 and 1998, only 4 were "clean" (i.e., not exceeding any screening value) (Figure 24).

Figure 24. Summary of stations with contaminant concentrations above screening values. Stations with no concentrations above screening values for any species sampled are unshaded. Stations with one or more concentrations above screening values are shaded. Data from this study and the SRWP (see figure 1).


## Recommendations

Long term monitoring should be conducted to track trends in contaminants of concern relative to screening values.

Contaminants found above screening values in this study (mercury, PCBs, DDT, dieldrin) should continue to be tracked. The data should be gathered that will allow OEHHA to decide whether or not a broader consumption advisory than the one currently in place for striped bass and sturgeon is warranted for the Delta.

Contaminants where existing data are inconclusive (arsenic, PAHs, toxaphene) should be analyzed using methods that would yield definitive comparisons with screening values.

Dioxin analysis should be incorporated into this monitoring to determine the spatial extent of screening value exceedances and to begin assessment of long term trends in dioxin concentrations. The analyses should include dioxins, dibenzofurans, and dioxin-like PCBs, all of which contribute to the overall dioxin-like potency of environmental samples.

Further Corbicula sampling should be included in this long term monitoring. Corbicula are relatively good accumulators of trace organics. Corbicula sampling is particularly effective for PAHs, since PAHs are quickly metabolized in fish. Corbicula also accumulated high concentrations of arsenic.

Further fish sampling should be conducted in the San Joaquin River watershed to characterize human health concerns related to chemical contamination.

Existing data suggest the lower San Joaquin River watershed is a focal point for organochlorine pesticide contamination. In addition, historic gold mining in this watershed is a potential source of mercury contamination. The spatial extent of screening value exceedances in this region should be characterized, examining the range of species that are popular with anglers.

## A fishery resource use study should be conducted in the Delta and Central Valley.

The Delta is a popular location for sport fishing, and a substantial subsistence fishing community is also thought to be present. A fishery resource use study would provide many benefits. First, it could identify human populations facing the greatest risk from consuming contaminated fish. This would improve our understanding of human health risks and guide outreach efforts to inform fishers of ways to reduce health risks. Second, the study could identify popular fishing locations and species. This information would be extremely valuable in effectively designing future sampling efforts.

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## Appendix—Data Tables

Table 1. Trace element concentrations in fish and clam tissue

Table 2. Pesticide concentrations in fish and clam tissue. Part 1 of 2 .
ng/g wet, surrogate corrected
$\mathrm{ND}=$ not detected or below reporting limit





















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