DEPARTMENT OF THE INTERIOR U.S. FISH AND WILDLIFE SERVICE REGION 1

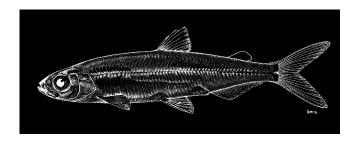
Tissue Residues and Hazards of Water-Borne Pesticides for Federally Listed and Candidate Fishes of the Sacramento-San Joaquin River Delta, California: 1993-1995

Study ID: 1130-1F18

Prepared by:

Jewel Bennett, Jana Hofius, Cathy Johnson, and Thomas Maurer

U. S. Fish and Wildlife Service Environmental Contaminants Division Sacramento Fish and Wildlife Office 2800 Cottage Way W-2605 Sacramento, CA 95825



Delta smelt (*Hypomesus transpacificus*)

July 2001

INTRODUCTION

The Sacramento-San Joaquin Delta is formed at the confluence of the south-flowing Sacramento River and the north-flowing San Joaquin River. The estuary encompasses 1,600 square miles, drains over 40 percent of the State of California, and provides habitat and stop over ground to numerous species of fish and wildlife. Two-thirds of salmon that migrate into California pass through the Delta, as do nearly half the migrating waterfowl and shorebirds. The Estuary, due to the world's largest manmade plumbing job, provides 7.2 million acre-feet of water a year for export, irrigates 4.5 million acres of farmland, and provides drinking water for 20 million Californians (SFEP, 1992).

The Delta provides habitat to many species of aquatic wildlife, including the federally-listed, threatened Delta smelt (*Hypomesus transpacificus*) and Sacramento winter-run chinook (*Oncorhynchus tschawytscha*) and the proposed-threatened longfin smelt (*Spirinchus thaleichthys*) and Sacramento splittail (*Pogonichthys macrolepidotus*). The shallow-edged, slower moving backwaters of the estuary provide optimal breeding and rearing habitat for the smelt, as well as numerous other species. Chinook salmon fry often spend a significant amount of time feeding and growing in the estuary before smoltification is complete and the young fish move to the ocean. This is especially true in wetter years. Other aquatic species dependent upon the watershed, also suffering severe population declines, include the recently listed California red-legged frog (*Rana aurora draytonii*), the tiger salamander (*Ambystoma tigrinum*), giant garter snake (*Thamnophis gigas*), and the western pond turtle (*Clemmys marmorata*).

Many fisheries are in a rapid decline in the Delta, smelt populations are estimated to have declined approximately 90% in the last 20 years. Of the original 29 indigenous fish species in the Delta, 12 have either been eliminated entirely, or are currently threatened with extinction (SFEP 1993). Populations declines are attributed to a combination of factors including increasing water diversions for export, loss of habitat, increased competition and predation from introduced species, and impaired water quality.

Delta smelt typically spawn between February and June (Figure 1). Smelt spawning areas include the lower sections of the Sacramento and San Joaquin Rivers. The early part of this period corresponds with the rainy season in the Central Valley of California, pesticide applications to orchards, alfalfa, and rice also peak during this time of the year (Figure 1) (Domagalski and Kuivila, 1991). Maximum contaminant concentrations are usually detected following rain events, when the rain flushes pesticides, mine drainage and urban runoff from soils and other media into the rivers via runoff. Connor *et al* (1993) found a significant seasonal component to aquatic toxicity when evaluating 414 samples collected during a $2\frac{1}{2}$ year study.

The Sacramento and San Joaquin Rivers receive agricultural drainwater from thousands of acres of irrigated farmland each year. According to the CA Department of Water Resources (1989), over 200 agricultural drains operate within the Delta alone. The drainwater contains elevated levels of agricultural pesticides, salts, and trace elements. Around 10 percent of the total U.S.

pesticide use occurs in these two watersheds each year. Approximately 14 and 55 million pounds of pesticides are applied each year in the Sacramento and San Joaquin watersheds respectively (Kuivila and Copeland 1993). Several pesticides (especially diazinon, chlorpyrifos, and carbofuran) are of particular concern because of their high volume of use, potential for runoff into surface waters, and high aquatic toxicity.

High concentrations of pesticides and aquatic toxicity have been measured in both the Sacramento and San Joaquin Rivers (Figure 2), their tributaries and the Delta in the recent past (Foe and Connor, 1991a, Foe and Connor, 1991b; Norberg-King *et al*, 1991; Finlayson *et al*, 1993; Bailey *et al*, 1994;). Some of the toxicity has been tied to agricultural practices associated with rice and alfalfa production and with dormant spray regimes in fruit and nut orchards. Pesticide concentrations are frequently documented at concentrations above the CA Department of Fish and Game's water quality criteria to protect aquatic life (California State Water Resources Control Board. 1984; Harrington, 1990; Menconi and Gray, 1992; Menconi and Harrington, 1992b; Menconi and Paul, 1994; Menconi and Cox, 1994). Erosion of soils also contribute soil-bound pesticides to the watersheds, including organochlorine products, used extensively in agriculture from the 1950s through the 1970s and early 1980s.

Waterways located around the periphery of the Sacramento-San Joaquin Delta were studied for toxicity from alfalfa pesticide use during March to April of 1992 (Foe and Sheipline, 1993). These locations received input from both rivers, as well as Delta agricultural fields. Thirteen percent of water samples were toxic to *Ceriodaphnia*. Diuron, diazinon, chlorpyrifos, and carbofuran were detected in these water samples.

In January of 1993, following rainstorms, the U.S. Geological Survey tracked a diazinon pulse in the Sacramento River that was measured at Freeport (89 river miles below most orchards) at 393 ng/L (Kuivila, 1993). One day later the pulse reached Rio Vista (43 miles further down stream) with a maximum concentration of 300 ng/L. Two days later the pulse was detected at Chipps Island (16.5 miles further downstream) with a maximum concentration of 200 ng/L, and finally, diazinon concentrations of 120 ng/L were detected five days later at Martinez (14.5 miles further downstream and toward the seaward edge of the Delta. In the same study, diazinon peaked in the San Joaquin River more quickly than in the Sacramento, and at higher concentrations. Following the first rain event, diazinon was measured at 773 ng/l and at 1,071 ng/l three days later (Kuivila, 1993). Samples collected in the San Joaquin River at Vernalis, exhibited 100% mortality to *C. Dubia* for twelve days following the first rain event.

Deanovic monitored sites twice monthly on the Sacramento and San Joaquin sides of the delta, between May 1993 and May 1994. Short-term chronic toxicity tests were run using *C. Dubia*, *Selenastrum capricornutum*, and fathead minnows. Sampling sites included the major rivers, back sloughs, and island drains. Out of 10 samples at each site, toxicity occurred in six of the Sacramento River samples, eight of the San Joaquin River samples (three at Vernalis and five at Antioch), seven of the Old River samples, one in the Middle River, and five in the Mokelumne River samples. The Port of Stockton, intended to represent an urban runoff-dominated system

had toxicity in four sampling events, the Delta-Mendota Canal also had toxicity in four samples (Bailey *et al*).

The Sacramento / San Joaquin Delta also receives periodic runoff from several abandoned mines, including Iron Mountain Mine, which was classified as a Superfund Site in 1983. Acid mine drainage (AMD) from the mine leaches metals and trace elements from surrounding substrates, frequently raising concentrations in the Sacramento River above aquatic life criteria. Copper, zinc and cadmium are the principal elements of concern. Historic placer mining activities for gold in the Sierra Nevada mountains have resulted in anthropogenically enriched mercury deposits. The coast range mountains have numerous mercury mines where mining activity left eroding tailings that also contribute mercury to the watershed. Mercury fish advisories have been issued for striped bass in the estuary, monitoring in the Bay has demonstrated that other edible fish also have elevated tissue concentrations of mercury (SF Regional Water Quality Control Board, 1994). Elevated mercury concentrations have also been detected in the Sacramento River, at Prospect Slough and in Cache Creek. Elevated mercury concentrations in water are generally highest after precipitation events.

Organochlorines (OCs) have been documented as significant problems in the Bay/Delta in numerous reviews conducted over the past 10 years. Philips, 1987, found that OCs were sufficiently high in localized areas to make adverse effects on biota likely. Montoya, 1991, reported that tissue concentrations of DDT, PCBs, and toxaphene exceeded criteria values in the lower Sacramento and San Joaquin Rivers, dieldrin concentrations exceeded criteria in the Sacramento River, and endosulfan and dicofol exceeded criteria in the San Joaquin River and Paradise Cut.

This report summarizes the results of three studies conducted by the U.S. Fish and Wildlife Service between 1994 and 1995. Biologists surveyed water and fish for metals, trace elements, and organics from the Sacramento and San Joaquin Rivers, to evaluate potential metal and trace element loading, and performed toxic identification evaluations (TIEs) on water from the back sloughs of the Delta. The studies were scoping in nature, designed to screen for potential problems and define the direction and focus of future investigations.

METHODS

Fish Tissue Analyses

Salvage Delta smelt (*Hypomesus transpacificus*) were obtained from the freezers of the California Department of Fish and Game (CDFG) in October 1994. The fish were caught in trawl nets during annual salmon abundance counts, mainly at Chipps Island at the western edge of the Sacramento/San Joaquin Delta (Figure 3). A few fish (less than five), were caught in the Sacramento River at Garcia Bend (Figure 3). The smelt used for contaminant analyses were those that had died in the nets before reaching the boat, thus they could not be returned to the water. Once on board, they were counted, measured, labeled, and bagged. The fish were frozen upon return to the lab each evening. Smelt were collected in May and June of 1993, and in April, May, and June of 1994.

Individual, whole-body delta smelt were analyzed for selenium and mercury, and composite egg samples were analyzed for selenium. Composite smelt samples were analyzed for aluminum, arsenic, boron, barium, beryllium, cadmium, chromium, copper, iron, mercury, magnesium, manganese, molybdenum, nickel, lead, selenium, strontium, vanadium, zinc, and scanned for organic contaminants. All samples were analyzed by atomic absorption spectroscopy, mercury by cold vapor reduction, selenium and arsenic by hydride generation, and metals by graphite furnace. Mercury detection limit was approximately .17 ug/g, As and Se were approximately 0.8 and 0.2 ug/g respectively.

Inland silversides were collected during beach seines in the San Joaquin River at Dos Reis State Park and Mossdale, California (Figure 3). Fish were measured at the site, bagged into individual or composite samples for metals analysis, and placed onto ice. Fish were frozen immediately upon return to the laboratory, within five hours of capture. Individual silversides were analyzed for copper, mercury, selenium and zinc. Composite samples were analyzed for aluminum, arsenic, boron, barium, beryllium, cadmium, chromium, iron, magnesium, manganese, molybdenum, nickel, lead, strontium, and vanadium, in addition to the previously mentioned constituents. Grab water samples were also collected at these two sites, preserved with nitric acid, and scanned for metal and trace element concentrations.

Water Toxicity

Sub-surface grab samples of water were collected weekly between May 2 and June 13, 1994, from back slough areas of the north delta (Figure 3) A total of 60 samples were collected and tested. Samples for bioassays were collected in pre-cleaned one gallon glass amber bottles and stored on ice while in the field. Samples for pesticide analyses were collected in one liter, amber, glass bottles and were acidified for pesticide analyses, placed on ice in the field and later stored at 4 degrees C.

Upon arrival at the UC Davis Aquatic Toxicology Laboratory (UCDATL), bioassay samples were stored in the dark at 4 degrees C. Bioassays were initiated within 24 hours of collection. Seven-day static renewal bioassays were conducted with *Ceriodaphnia dubia* (*C. dubia*). Bioassay procedures followed EPA guidelines for 3-species chronic toxicity testing (EPA, 1989).

Bioassays were initiated with <24-hour-old C. dubia obtained from established cultures at the UCDATL. C. dubia were cultured in well water diluted with glass distilled water to EPA moderately hard specifications. C. dubia were exposed in 29 mL gass scintillations vials. Each treatment consisted of 10 replicate bials containing on < 24-hour-old neonate in 18 mLs of test solution. Test solutions were renewed daily. Ceriodaphnids were fed a mixture of trout chow and green algae. Test temperatures were 25 ± 1 degree C. Test endpoints were mortality and young production.

Test mortality was compared to the control using Fisher's Exact Test (DiGiorgio et al., 1994). In cases where parametric assumptions were met, young production was compared to the control

using ANOVA followed by Dunnett's multiple comparison test, or in the case of unequal sample sizes, Bonferroni t-test (EPA, 1989). In cases where parametric assumptions were no met a Kruskal-Wallis test followed by Steel's Many One-Rand or Wilcoxin Signed-Rank test was used (EPA, 1989).

RESULTS

Delta smelt mean body burdens (Table 1, Table 2) of copper and mercury were above the EDL $_{95}$ (Elevated Data Level). The EDL $_{95}$ represents the 95 percentile concentration of each respective concentration found in all fish collected statewide by the Toxic Substances Monitoring Program, conducted by the CA State Water Resources Control Board, between 1978 and 1993 (CA SWRCB, 1995). Mean copper concentration in three composite smelt samples was 22.3 ppm \pm 2.5. Mean mercury concentration in 14 individual smelt was 0.60 ppm \pm 0.21. Whole body nickel (0.7 \pm 0.4 ppm) and zinc (132 \pm 8 ppm) concentrations were above the EDL $_{85}$, chromium levels (0.59 \pm 0.09 ppm) approached the EDL $_{85}$. Selenium levels (1.5 \pm 0.3 ppm) were within normal range.

Organic analyses on smelt composites revealed elevated body burdens of various napthalene derivatives. The form with the highest concentration was C1-naphthalene, at 240 μ g/kg. Total PCBs, DDE and DDD, ∞ -chlordane and toxaphene, and trans-nonachlor were also elevated in the smelt samples (Table 4).

Results from Inland silversides, collected in the San Joaquin River, were markedly different from the Sacramento River Delta smelt. Silversides, like the smelt, are a short-lived fish that feed primarily on zooplankton. Although their foraging behavior and life histories differ somewhat, the non-native silversides is often used as a surrogate for the smelt. Silversides were above the EDL_{85} for chromium and mercury (Table 2). Barium, magnesium, and selenium concentrations were also higher in the silversides than in smelt. Aluminum, cadmium, copper, nickel, lead, vanadium, and zinc were higher in smelt than in the silversides. Concentrations of arsenic, boron, beryllium, iron, mercury, magnesium, molybdenum, and strontium were similar in the two species. Mercury concentrations were above the EDL_{85} in both species.

Silversides and water samples were collected once-a-month for three months (April, May, July, 1995). Body burdens of aluminum, chromium, copper, iron, magnesium, manganese, and zinc appear to trend upward in the fish as the months progress (Table 3). Analyses of water samples collected during the smelt seines detected no elevated metals or trace elements.

Only one water sample collected from the Delta back sloughs by the Service exhibited significant toxicity to *Ceriodaphnia* (Table 4). A sample collected in Sycamore Slough on 5/23/94 exhibited 44% *Ceriodaphnia* mortality. TIEs were attempted, but the causative agent was not identified. Reproduction of *Ceriodaphnia* was not affected by any of the back slough waters collected in the delta. Organochlorine and carbamate scans on the water samples yielded

no detectable residues. Organophosphate scans were originally requested, however they were inadvertently omitted from the final catalog and unfortunately not conducted.

DISCUSSION

Fish mercury concentrations were elevated in both the Sacramento and the San Joaquin Rivers. Delta smelt in the Sacramento River had 600 µg/kg whole body mercury concentration. Silversides in the San Joaquin River also had 600 µg/kg in July, averaged over the 3 months of collection the silversides mercury concentration was 430 µg/kg. It is generally assumed that nearly all of the mercury in fish is methyl mercury. Eisler, 1987, recommends food items for avian predators not exceed 100 µg/kg. The National Academy of Sciences (NAS) mercury guideline to protect fish and their predators is 500 µg/kg (WW) (NAS, 1973). Although these fishes were not quite at the NAS guideline, both species in this report are one-year fish, so mercury is being accumulated quite rapidly. The July silversides actually appeared to be young of the year, as they were so small that the analyses had to be run of composite samples to produce enough tissue mass. In this case, the fish are accumulating elevated levels within a few months of hatching, or possibly carrying burdens passed on to them, in the egg, from their parent. The toxicological significance of these body burdens is unknown, however, toxicity studies on fish have reported inhibition of reproduction, respiratory impairment, disruption of the osmoregulatory function of the gills (Burton et al, 1972; Evans, 1987), reduction of monoamine and cholinesterase activities in neural tissue (Kirubagaran and Joy, 1990; Shaw and Panigrahi, 1990), reduction of acid and alkaline phosphatase activity responsible for liver and kidney membrane transport (Hinton and Loenig, 1975; Lakshmi et al, 1991), adverse effects on liver and muscle protein synthesis (Nicholls et al, 1989), and disruption of a number of other essential biochemical processes, all associated with mercury exposure in fish.

Of equal concern to the toxicological threat the mercury burdens may pose to the fish themselves, is the toxicological threat that these fish may pose to the predatory fish that eat them. Six hundred parts-per-billion methyl mercury consumed many times per day, day after day, can translate into a substantial mercury burden to higher trophic level fish. Mercury concentrations in lake trout have been shown to be related to trophic position and food-web structure (Futter, 1994), Hall *et al*, 1994, experimentally confirmed the dietary route of exposure as the most important one for fish. The half-life of methyl mercury in fish muscle is estimated at 2-3 years (Sorensen, 1991).

Fish size is also important in mercury sensitivity, smaller fish are more susceptible than larger fish. Smaller fish also tend to accumulate mercury at greater rates than larger fish due to their higher metabolic rates (Reinert et al, 1974).

Bioconcentration factors from water to silversides in Clear Lake, CA were in the range of 10^4 to 10^5 for total mercury, and 10^6 to 10^7 for methyl mercury. Large mouth bass concentrations were 26-fold higher than silversides (Suchanek, 1994).

Selenium concentrations in the silversides are probably at the upper end of the range for normal background concentrations in various fish species (Skorupa *et al*, 1996, Lemly 1993b). Skorupa reports normal wholebody selenium as <1 - 4 ppm, with concentrations typically less than two. Mean selenium concentrations in the silversides ranged between 2.2 and 2.9. Skorupa estimates a true threshold range for reproductive impairment in sensitive species as between 4 and 6 ppm whole body concentration.

Saiki *et al*, 1995 cite normal background levels of copper, cadmium, and zinc as <0.20, <0.021, and 4.24 mg/kg (ww) respectively, in rainbow trout. Delta smelt in this study had ww copper concentrations of 6.5, over 32 times higher than published "normal background". Cadmium in the smelt was 0.03, and zinc was 39, almost 10 fold greater than the rainbow trout. The primary target for the toxic action of copper to freshwater fish is thought to be the gill ion regulatory apparatus, followed by gill damage and ultimately respiratory toxicity as a result of physical damage to the gills (Wilson and Taylor, 1993). Fish adapted to 33% seawater were much less susceptible to copper toxicity than fresh water fish. The implications of this to the brackish water smelt are unknown, they may be better able to tolerate higher copper concentrations than other fish.

Aromatic hydrocarbons, of which naphthalene is frequently used as a model, are potential carcinogens, and have been shown to adversely impact growth, reproduction, and survival (REFS). Tjeerdema and Crosby evaluated the bioconcentration and metabolic fate of napthalene in Delta striped bass (*Morone saxatilis*) in 1993. They found that the bass rapidly accumulated naphthalene, with a 24-hr BCF of 283.7, and slowly depurated it. The skin contained the greatest fraction of the retained naphthalene residues (44.5%), however, when the bass where removed from the contaminated test chambers and allowed to depurate, concentrations sequestered in the viscera/gonads actually increased when all other tissue levels significantly declined. The potential for naphthalene to act a reproductive toxicant to smelt and other Delta fisheries is unclear, but as a cumulative stressor to an already stressed fish, there may be an impact. The ability of the smelt to metabolize naphthalene to a more hydrophilic compound, and thus increase its excretion efficiency is also unknown, but if Phase I oxidation activity is low or non-inducible in smelt gonads, it could contribute to an even greater accumulation in the reproductive tissues. The authors also found an increasing susceptibility of striped bass to naphthalene with increasing water salinity.

That no pesticides were detected in our temporally- limited sampling events only means they were not present at those particular points in time. This is not altogether surprising, as May-June are not at the height of the pesticide application process, and since the sampling did not follow rain events, there was no flushing action to move the pesticides off-site. That one sample resulted in 44% *Ceriodaphnia* mortality, under these conditions, is an indication that pesticides are lurking in this eco-system. Many other studies have conclusively reported and defined pesticide toxicity in the Delta.

SUMMARY and CONCLUSIONS

- Whole-body mercury concentrations are elevated in both Delta smelt in the Sacramento River and inland silversides in the San Joaquin River. Further research is needed to determine potential impacts to these and predatory fish populations from these body burdens.
- Copper concentrations are over 30 times higher than normal published background concentrations in Delta smelt in the Sacramento River. Zinc is 10 times higher than normal background for rainbow trout.
- Naphthalene concentrations may be elevated in Delta smelt. The source and potential impacts to smelt reproduction need to be evaluated.
- Although detectable concentrations of pesticides were not found in this study, it is probably only a reflection of the timing and weather conditions associated with this particular sample collection regime. Pesticide residues remain a potential risk to aquatic Bay/Delta communities at other times of the year.

Table 1. Delta smelt and Inland Silversides metal and trace element body burdens. Smelt collected at Chipps Island during the springs of 1993 and 1994. Silversides collected in San Joaquin River, May-July 1995.

| | | Delta Smelt | | | Inland Silverside | |
|------------|--------|---------------------|-------------|----|--|------------------|
| Analyte | n | $ppm (dw) \pm S.D.$ | Range | n | ppm (dw) ± S.D. | Range |
| Aluminum | 3 | 162 ± 69 | 85 - 220 | 9 | 79.2 ± 59.7 | 36.4 - 215 |
| Arsenic | 3 | 0.91 ± 0.28 | 0.65 - 1.2 | 9 | 0.99 ± 0.17 | 0.73 - 1.21 |
| Boron | 3 | ND | | 9 | ND | |
| Barium | 3 | 4.7 ± 0.9 | 4 - 5.7 | 9 | 11.4 ± 3.5 | 7.11 - 17.7 |
| Beryllium | 3 | ND | | 9 | ND | |
| Cadmium | 3 | 0.11 ± 0.02 | 0.1 - 0.13 | 9 | ND | |
| Chromium | 3 | 0.59 ± 0.09 | 0.5 - 0.67 | 9 | 1.6 ± 0.8 | 0.5 - 2.65 |
| Copper | 3 | 22.3 ± 2.5 | 20 - 25 | 24 | 2.13 ± 0.5 | 1.43 - 2.98 |
| Iron | 3 | 198 ± 94 | 101 - 288 | 9 | 122.5 ± 75.2 | 66.6 - 301 |
| Mercury | 1 7 | 0.6 ± 0.21 | 0.36 - 0.77 | 24 | 0.43 ± 0.15 | 0.238 - 0.742 |
| Magnesium | 3 | 1347 ± 142 | 1220 - 1500 | 9 | 1402.4 ± 99.8 | 1303 - 1565 |
| Manganese | 3 | 9.8 ± 1.6 | 8.7 - 11.6 | 9 | 22.6 ± 5.6 | 18.2 - 36.2 |
| Molybdenum | 3 | ND | | 9 | ND | |
| Nickel | 3 | 0.7 ± 0.4 | 0.4 - 1.1 | 9 | ND | |
| Lead | 3 | 0.1 ± 0.1 | 0.1 - 0.2 | 9 | ND* | |
| Selenium | 4 | 1.5 ± 0.3 | 0.7 - 2.3 | 58 | 2.58 ± 0.45 | 1.6 - 3.4 |
| Strontium | 3 | 70.6 ± 20.8 | 53 - 94 | 9 | 74.8 ± 8.7 | 59.1 - 89.0 |
| Vanadium | 3 | 0.9 ± 0.2 | 0.6 - 1 | 9 | ND | |
| Zinc | 3 | 132 ± 8 | 123 - 139 | 24 | 102.3 ± 19.0 | 79.3 - 155 |

^{*}one fish at 0.97 ppm

Table 2 - Delta smelt and inland silversides constituent concentrations and Toxic Substance Monitoring Program elevated data levels.

| Analyte | Delta smelt ppm (WW) | silversides ppm (WW) | EDL |
|----------|-------------------------|-------------------------|-----------|
| Arsenic | 0.26 | 0.22 | 0.44 (85) |
| Chromium | 0.17 | 0.34 | 0.23 (85) |
| Copper | 6.5 | 0.46 | 3.41 (85) |
| Mercury | 0.18 | 0.10 | 0.15 (95) |
| Nickel | 0.2 | ND | 0.2 (85) |
| Selenium | 0.51 | 0.58 | 1.5 (85) |
| Zinc | 39 | 22 | 40 (85) |

Table 3 - Body burdens of metals and trace elements, by month, in inland silversides captured in the San Joaquin River.

| | April '95 | | May '95 | July '95 |
|------------|-----------|-------------------|-----------------|-----------------|
| Analyte | n | ppm (dw) ± S.D | ppm (dw) ± S.D | ppm (dw) ± S.D |
| Aluminum | 3 | 37.5 ± 1.1 | 54.6 ± 15.5 | 145 ± 62.8 |
| Arsenic | 3 | 0.99 ± 0.17 | 0.93 ± 0.25 | 1.06 ± 0.1 |
| Boron | 3 | ND | ND | ND |
| Barium | 3 | 8.3 ± 1.4 | 13.6 ± 4.2 | 12.2 ± 2.5 |
| Beryllium | 3 | ND | ND | ND |
| Cadmium | 3 | ND | ND | ND |
| Chromium | 3 | 0.7 ± 0.3 | 1.7 ± 0.5 | 2.4 ± 0.4 |
| Copper | 5 | 1.6 ± 0.2 | 2.3 ± 0.4 | 2.6 ± 0.4 |
| Iron | 3 | 66.9 ± 0.3 | 100 ± 16.5 | 200 ± 88.8 |
| Mercury | 5 | 0.28 ± 0.03 | 0.60 ± 0.06 | 0.40 ± 0.04 |
| Magnesium | 3 | 1336 ± 53 | 1355 ± 14 | 1517 ± 84 |
| Manganese | 3 | 19.9 ± 1.5 | 22.3 ± 3.7 | 25.7 ± 9.2 |
| Molybdenum | 3 | ND | ND | ND |
| Nickel | 3 | ND | ND | ND |
| Lead | 3 | ND | ND | .97 (one fish) |
| Selenium | 15 | 2.93 ± 0.3 | 2.6 ± 0.2 | 2.2 ± 0.5 |
| Strontium | 3 | 79.9 ± 2 | 79.2 ± 8.5 | 65.4 ± 5.4 |
| Vanadium | 3 | ND | ND | ND |
| Zinc | 3 | 105 ± 9.7 | 96.1 ± 10.7 | 129 ± 17.0 |

Table 4 - Organic contaminant concentrations in composite Delta smelt samples.

| Analyte | Result ppb (dw) | NAS Guideline ppb (ww) |
|-----------------------------|-----------------|------------------------------|
| 1,2,5,6-dibenzanthrace ne | ND | |
| 1,2-benzanthracene | ND | |
| 1-methylnaphthalene | 80 | |
| 1-methylphenanthrene | ND | |
| 2,3,5-trimethylnaphtha lene | ND | |
| 2,6-dimethylnaphthal ene | 40 | |
| 2-methylnaphthalene | 160 | |
| C1-Fluoranthenes & Pyrenes | ND | |
| C1-chrysenes | ND | |
| C1-dibenzothiophenes | ND | |
| C1-fluorenes | ND | |
| C1-naphthalenes | 240 | |
| C1-phenanthrenes | ND | |
| C2-chrysenes | ND | |
| C2-dibenzothiophenes | ND | |
| C2-fluorenes | ND | |
| C2-naphthalenes | 40 | |
| C2-phenanthrenes | ND | |
| | | |

Table 4 - Organic contaminant concentrations in composite Delta smelt samples.

| C3-chrysenes | ND | |
|----------------------|-----|-----|
| C3-dibenzothiophenes | ND | |
| C3-fluorenes | ND | |
| C3-naphthalenes | ND | |
| C3-phenanthrenes | ND | |
| C4-chrysenes | ND | |
| C4-naphthalenes | ND | |
| C4-phenanthrenes | ND | |
| НСВ | ND | |
| PCB-TOTAL | 200 | 500 |
| acenaphthalene | ND | |
| acenaphthene | ND | |
| alpha BHC | ND | |
| alpha chlordane | 40 | |
| anthracene | ND | |
| benzo(a)pyrene | ND | |
| benzo(b)fluoranthene | ND | |
| benzo(e)pyrene | ND | |
| benzo(g,h,i)perylene | ND | |
| benzo(k)fluoranthene | ND | |
| beta BHC | ND | |
| biphenyl | ND | |
| chrysene | ND | |
| cis-nonachlor | ND | |
| delta BHC | ND | |

Table 4 - Organic contaminant concentrations in composite Delta smelt samples.

| dibenzothiophene | ND | |
|----------------------------|-----------|----------|
| dieldrin | ND | |
| endosulfan I | ND | |
| endosulfan II | ND | |
| endosulfan sulfate | ND | |
| endrin | ND | |
| fluoranthene | ND | |
| fluorene | ND | |
| gamma BHC | ND | |
| gamma chlordane | ND | |
| heptachlor epoxide | ND | |
| indeno(1,2,3-cd)pyren e | ND | |
| mirex | ND | |
| naphthalene | 160 | |
| o,p'-DDD | ND | |
| o,p'-DDE | ND | |
| o,p'-DDT | ND | |
| oxychlordane | ND | |
| p,p'-DDD | 80 | Total |
| | | DDT 1000 |
| p,p'-DDE | 120 | DDT 1000 |
| p,p'-DD E p,p'-DDT | 120 ND | DDT 1000 |
| | | DDT 1000 |
| p,p'-DDT | ND | DDT 1000 |

Table 4 - Organic contaminant concentrations in composite Delta smelt samples.

| toxaphene | 200 | 100 |
|-----------------|-----|-----|
| trans-nonachlor | 40 | |

Table. 5 - Water quality and *Ceriodaphnia* toxicity test results for the Sacramento-San Joaquin Rivers delta water sampling study May 2 through June 13, 1994.

| Site | Location Name | Date 1994 | Water Temp. C ° | рН | D.O. mg/L | Spec. Cond. us/L | Salinit y % | 96-hr Toxicit y % | 7-day Toxicit y % |
|------|--------------------|------------------------------------|------------------------------|--------------------------|---------------------------|---------------------------|---------------------------|----------------------------|----------------------------|
| A | Beaver Slough | May 2 May 9 May 16 May 23 | 18.0 18.8 19.2 20.5 | 7.7 7.7 7.5 7.8 | 9.2 8.6 7.9 8.3 | 197 171 136 213 | 0.2 0.2 nd 0.1 | 0 0 0 0 | 0 0 0 0 |
| В | Beaver Slough | May 2 May 9 May 16 May 23 | 18.2 19.2 19.3 21.2 | 7.9 7.6 7.5 7.7 | 9.3 8.8 7.6 7.8 | 232 254 211 271 | nd 0.03 0.05 0.2 | 0 0 0 0 | 0 0 0 |
| С | Beaver Slough | May 2 May 9 May 23 | 18.6 19.2 21.2 | 8.2 7.6 7.8 | 9.8 8.3 8.3 | 283 221 260 | 0.02 0.02 0.4 | 0 0 0 | 0 0 0 |
| J | Beaver Slough | May 16 | 18.9 | 8.7 | 7.8 | 245 | 0.05 | 0 | 0 |
| D | Hog Slough | May 2 May 9 May 16 May 23 | 18.8 18.9 18.2 21.2 | 7.8 7.6 8.4 8.0 | 9.5 8.5 8.9 8.3 | 321 352 342 360 | 0 0.02 0.5 0 | 0 0 0 0 | 0 10 0 10 |
| Е | Hog Slough | May 2 May 9 May 16 May 23 | 21.5 19.5 19.1 21.6 | 8.6 8.0 8.6 8.5 | 10.7 7.8 8.6 8.9 | 493 548 463 423 | nd 0.02 0.5 0 | 0 0 0 0 | 0 0 0 0 |
| F | Hog Slough | May 2 May 9 May 16 May 23 | 17.9 19.8 18.9 21.3 | 7.4 8.0 8.6 8.5 | 8.8 7.7 7.5 10.1 | 888 630 578 1000 | 0 0.03 0.5 0 | 0 0 0 0 | 0 0 0 0 |
| G | Sycamore Slough | May 2 May 9 May 16 May 23 | 18.9 20.1 18.9 22.0 | 8.1 8.4 8.5 8.6 | 9.8 10.2 8.7 9.2 | 269 270 264 259 | nd 0 0.4 0 | 0 0 0 10 | 0 10 10 10 |
| Н | Sycamore Slough | May 2 May 9 | 19.1 20.5 | 8.5 8.6 | 10.7 10.8 | 268 268 | nd 0.03 | 0 | 0 |

Table. 5 - Water quality and *Ceriodaphnia* toxicity test results for the Sacramento-San Joaquin Rivers delta water sampling study May 2 through June 13, 1994.

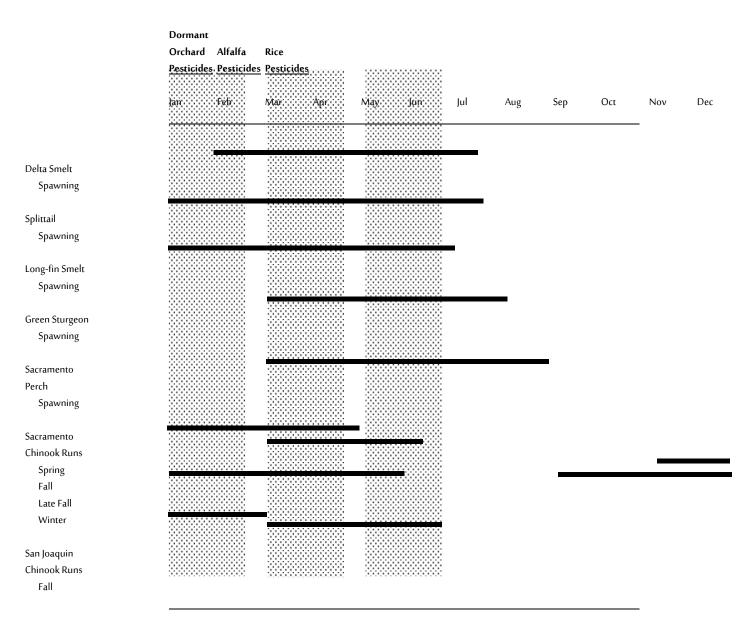
| | 1 | M 16 | 10.4 | 0.7 | 0.0 | 260 | 0.4 | 0 | 10 |
|---|---------------------|---------|--------------|------------|-------------|------------|------|----|---------|
| | | May 16 | 19.4 23.4 | 8.7 8.8 | 9.0 10.0 | 268 264 | 0.4 | 0 | 10 0 |
| | | May 23 | 23.4 | 0.0 | 10.0 | 204 | U | U | U |
| I | Sycamore | May 2 | 19.6 | 9.1 | 13.5 | 215 | 0.1 | 0 | 0 |
| | Slough | May 9 | 21.0 | 8.4 | 9.7 | 237 | 0.02 | 0 | 0 |
| | | May 16 | 18.3 | 8.4 | 8.7 | 278 | 0.4 | 0 | 0 |
| | | May 23 | 23.3 | 7.4 | 6.9 | 140 | 0 | 0 | 44 |
| K | So. Fork | May 2 | 18.9 | 7.6 | 9.3 | 263 | 0 | 0 | 0 |
| | Mokelumne | May 9 | 19.2 | 7.8 | 9.0 | 273 | 10 | 10 | 10 |
| | River | May 16 | 19.3 | 8.6 | 9.7 | 229 | 0 | 0 | 0 |
| | | May 23 | 20.7 | 8.1 | 9.3 | 276 | 0 | 0 | 0 |
| L | Sacramento River | June 6 | 20.6 | 8.0 | 9.0 | 230 | nd | 0 | 0 |
| М | Cache Slough | June 6 | 20.1 | 7.5 | 8.0 | 208 | nd | 0 | 0 |
| N | Lindsey | June 6 | 19.4 | 7.0 | 6.4 | 519 | 0.1 | 0 | 0 |
| | Slough | June 13 | 21.3 | 7.3 | 7.3 | 290 | nd | 0 | 0 |
| О | Lindsey Slough | June 6 | 20.6 | 7.9 | 9.1 | 265 | 0 | 0 | 0 |
| P | Lindsey Slough | June 6 | 19.9 | 7.8 | 8.9 | 282 | 0 | 0 | 0 |
| Q | Hastings | June 6 | 20.5 | 7.5 | 7.3 | 282 | nd | 0 | 0 |
| | Cut | June 13 | 21.1 | 7.7 | 7.3 | 289 | nd | 0 | 0 |
| R | Barker Slough | June 6 | 19.7 | 7.6 | 7.2 | 284 | 0 | 0 | 0 |
| S | Cache | June 6 | 19.6 | 7.8 | 8.5 | 288 | 0 | 0 | 0 |
| | Slough | June 13 | 21.3 | 7.4 | 8.0 | 220 | nd | 0 | 0 |
| Т | Lookout Slough | June 6 | 22.1 | 7.8 | 8.6 | 257 | nd | 0 | 0 |
| U | Shag | June 6 | 20.4 | 7.9 | 8.6 | 222 | nd | 0 | 0 |
| | Slough | June 13 | 22.2 | 7.4 | 8.0 | 291 | nd | 0 | 0 |
| | | June 13 | 20.8 | 7.8 | 8.3 | 254 | nd | 0 | 0 |
| | Prospect | June 13 | 21.3 | 7.5 | 8.2 | 275 | nd | 0 | 0 |

Table. 5 - Water quality and *Ceriodaphnia* toxicity test results for the Sacramento-San Joaquin Rivers delta water sampling study May 2 through June 13, 1994.

| Slough | June 13 | 20.5 | 7.6 | 7.0 | 363 | nd | 0 | 0 |
|--------|---------|------|-----|-----|-----|----|---|---|
| | June 13 | 21.8 | 7.4 | 8.2 | 251 | nd | 0 | 0 |
| | June 13 | 21.9 | 7.6 | 8.5 | 242 | nd | 0 | 0 |
| | June 13 | 21.9 | 7.3 | 8.4 | 228 | nd | 0 | 0 |

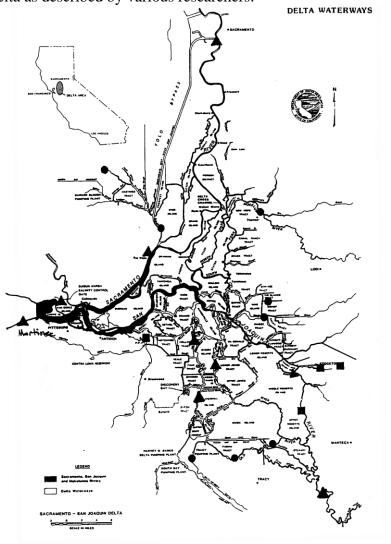
nd - not determined

Figure 1. Phenology of pesticide use and activities of federally listed, candidate, and declining fishes in the Sacramento-San Joaquin Delta.



Note: Chinook salmon activity indicates when juveniles are likely to be emigrating down the rivers and through the Delta.

Figure 2. Locations of acutely toxic pesticide concentrations or aquatic toxicity events in the Sacramento and San Joaquin Rivers Delta as described by various researchers.



- Ceriodaphnia toxicity during 1991-92 alfalfa season sprays (Foe and Sheipline 1993)
- Ceriodaphnia toxicity during 1991-92 orchard dormant sprays (Foe and Sheipline 1993)
- Acutely toxic concentrations of diazinon during 1993 orchard dormant sprays (Kuivila and Copeland 1993, and Kuivila et al. 1993)

REFERENCES

- Bailey, H.C., S. Clark, J. Davis, and L. Wiborg. The Effects of Toxic Contaminants in Waters of the San Francisco Bay and Delta. Final Report prepared for the Bay/Delta Oversight Council. Dept. of Water Resources, Contract No. B-59645.
- Bailey, H.C., C. Alexander, C. Digiorgio, M.Miller, S.I. Doroshov, and D.E. Hinton, 1994. The effect of agricultural discharges on striped bass (*Morone saxatilis*) in California's Sacramento-San Joaquin drainage. Ecotoxicology 3:123-142.
- Burton, D.T., A.H. Jones, J. Cairns, Jr.,1972. Acute zinc toxicity to rainbow trout (*Salmo gairdneri*): confirmation of the hypothesis that death is related to tissue hypoxia. J Fish Res Board Can 29:1463-1466.
- CA Department of Water Resources (DWR), 1989. The Delta as a Source of Drinking Water. Department of Water Resources, Central District, Interagency Delta Health Aspects Monitoring Program, Sacramento, CA.
- California State Water Resources Control Board. 1984. Rice herbicides: molinate and thiobencarb: Special Projects Report No. 84-4sp. 176 pp.
- CA SWRCB (State Water Resource Control Board). 1995. Toxic Substances Monitoring Program, 1992-1993 Data Report. Prepared by Del Rasmussen. Report 95-1WQ, May 1995.
- DiGiorgio, C., H. C. Bailey and D. E. Hinton. 1994. Delta Water Quality Monitoring Program.
- Connor, V., C. Foe, and L. Deanovic, 1993. Sacramento River Basin Biotoxicity Survey Results 1988-1990. Central Valley Regional Water Quality Control Board, Sacramento, CA.
- Domagalski, J.L. and K.M. Kuivila, 1991. Transport and transformation of dissolved rice pesticides in the Sacramento River Delta, CA. U.S. Geological Survey Open-file Report 91-227.
- Eisler, R., 1987. Mercury Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. Biological Report 85(1.10).90 pp.
- EPA, 1989. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms, 2nd edition. EPA/6004-89/001. 249 pgs.
- EPA, 1986. Ambients water quality criteria for Toxaphene. U.S. Environmental Protection Agency, Publication 440/5-86-006. 85pp.
- Evans, D.H., 1987. The fish gill: Site of action and model for toxic effects of environmental pollutants. Environ Health Perspect 71:47-58.

- Finlayson, B.J., J.A. Harrington, R. Fujimura, and G. Issac, 1993. Identification of methyl parathion in Colusa Basin Drain water. Env. Tox. and Chem. 12:291-303.
- Foe, C.G., and V. Connor, 1991a. 1989 Rice season toxicity monitoring results. Staff report Central Valley Regional Water Quality Control Board, Sacramento, CA.
- Foe C.G., and V. Connor, 1991b. San Joaquin watershed bioassay results, 1988-90. Staff report. Central Valley Regional Water Quality Control Board, Sacramento, CA.
- Foe, C. and R. Sheipline. 1993. Pesticides in surface water from applications on orchards and alfalfa during winter and spring of 1991-1992. Report of the California Regional Water Quality Control Board, Central Valley Region. 162 pp.
- Futter, M.N., 1994. Pelagic food-web structure influences probability of mercury contamination in lake trout (*Salvelinus namaycush*). Sci Total Env 145:7-12.
- Hall, B.D., R.A. Bodaly, R.J.P. Fudge, J.W.M. Rudd, 1994. Food as the dominant pathway of methylmercury uptake by fish. Presentation to the International Conference on Mercury as a Global Pollutant. July 10-14, 1994. Whistler, British Columbia.
- Harrington, J.M., 1990. Hazard Assessment of the Rice herbicides Molinate and Thiobencarb to aquatic organisms in the Sacramento River System. CA Department of Fish and Game, Environmental Services Division, Sacramento, CA.
- Hinton, D. and J.C. Koening, 1975. Acid phosphatase activity in the subcvellular fractions of fish liver exposued to methylmercury chloride. Comp Biochem Physiol 50:621-625.
- Kirubagaran R., and K.P. Joy, 1990. Changes in brain monoamine levels and monoamine oxidase activity in the catfish, *Clarias batrachus*, during chronic treatments with mercurials. Bull Environ Contam Toxicol 45:88-93.
- Kuivila, K.M., 1993. Diazinon concentrations in the Sacramento and San Joaquin Rivers and San Francisco Bay, California, February 1993. U.S.Geological Survey open-file report 93-440.
- Kuivila, K. M. and D. D. Copeland. 1993. Diazinon concentrations and transport in the Sacramento River and San Francisco Bay, California, February 1993. Preliminary Report. U.S. Geological Survey, Sacramento, CA. 15 pp.
- Lakshmi, R., R. Kundu, E. Thomas, and A.P. Mansuri, 1991. Mercuric chloride induced inhibition of acid and alkaline phosphatase activity in the kidney of mudskipper, *Boleophthalmus dentatus*. Acta Hydrochim Hydrobiol 19:341-344.
- Lemly, A.D., 1993b. Teratogenic effects of selenium in natural populations of freshwater fish. Ecotox Environ Safety 32:181-204.

- Menconi, M. and C. Cox, 1994. Hazard Assessment of the insecticide Diazinon to aquatic organisms in the Sacramento-San Joaquin River System. CA Department of Fish and Game, Environmental Services Division, Sacramento, CA.
- Menconi, M. and A. Paul 1994. Hazard Assessment of the insecticide Chlorpyrifos to aquatic organisms in the Sacramento-San Joaquin River System. CA Department of Fish and Game, Environmental Services Division, Sacramento, CA.
- Menconi, M. and J. M. Harrington, 1992b. Hazard Assessment of the insecticide Methyl Parathion to aquatic organisms in the Sacramento River System. CA Department of Fish and Game, Environmental Services Division, Sacramento, CA.
- Menconi, M. and S. Gray, 1992. Hazard Assessment of the insecticide Carbofuran to Aquatic Organisms in the Sacramento River System. CA Department of Fish and Game, Environmental Services Division, Sacramento, CA
- Montoya, 1991. An analysis of the toxic water quality impairments in the Sacramento/ San Joaquin Delta/Estuary. Central Valley Regional Water Quality Control Board, staff report. Sacramento, CA.
- National Academy of Sciences-National Academy of Engineering, 1973. Water Quality Criteria, 1972 (Blue Book). U.S. Environmental protection Agency, Ecological Research Series.
- Nicholls, D.M., D. Teichert-Kuliszewska, and G.R. Girgis, 1989. Effect of chronic mercuric chloride exposure on liver and muscle enzymes in fish. Comp Biochem Physiol 94C:265-270.
- Norberg-King, T.J., E.J. Durham, B.T. Ankley, and E. Robert, 1991. Application of toxicity identification evaluations procedures to the ambient water of the colusa Basin Drain, California. Env. Tox. and Chem. 10:891-900.
- Philips, D.J.H., 1987. Toxic Contaminants in the San Francisco Bay-Delta and their possible biological effects. SF Bay-Delta Aquatic Habitat Institute, Richmond, Ca.
- Reinert, R.E., L.J. Stone, and W.A. Willford. 1974. Effect of temperature on accumulation of methylmercuric chloride and p,p'-DDT by rainbow trout (Salmo gairdneri). J. Fish. Res. Board Can. 31:1649-1652.
- Saiki, M.K., D.T. Castleberry, T.W. May, B.A. Martin, and F.N. Bullard, 1995. Copper, cadmium, and zinc concentrations in aquatic food chains from the upper Sacramento River (California) and selected tributaries. Arch Env Contam and Tox 29:484-491.
- SFEP (San Francisco Estuary Project), 1993. Comprehensive Conservation and Management Plan. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.
- SFEP (San Francisco Estuary Project). 1992. State of the estuary. A report on conditions and problems in the San Francisco Bay / Sacramento-San Joaquin Delta Estuary. June 1992. 270 pp.

- Shaw, B.P. and A.K. Panigrahi, 1990. Brain AchE activity studies in some fish species collected from a mercury contaminated estuary. Water Air Soil Pollut 53:327-334.
- Skorupa, J.P., S.P. Morman, and J.S. Sefchick-Edwards, 1996. Guidelines for Interpreting Selenium Exposures of Biota associated with Nonmarine Aquatic Habitats. U.S. Fish and Wildlife Service Staff Report, prepared for the National Irrigation Water Quality Program.74 pp.
- Sorensen, E., 1991. Metal Poisoning in fish. Chapter VIII, Mercury. CRC Press, Boca Raton, FL. pp. 285-330.
- Suchanek, T., P. Richerson, L. Woodward, D. Slotton, L. Holts, C.E.E. Woodmansee, 1993. Ecological Assessment of Sulphur Bank Mercury mine superfund site, Clear Lake, CA. Preliminary Lake Study Report. 113 pp.
- Tjeerdema, R.S., and D.G. Crosby. Bioconcentration and metabolic fate of a Petroleum-based hydrocarbon in striped bass. Final Research Report.
- Wilson, R.W. and E. W. Taylor, 1993. Differential responses to copper in rainbow trout (*Oncorhynchus mykill*) acclimated to sea water and brackish water. Jour Comp Phys 163B:239-246.