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National Water-Quality Assessment Program

Concentrations of Chlorinated Organic Compounds in Biota and Bed Sediment in Streams of the Lower San Joaquin River Drainage, California

Open-File Report 98-171

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BY LARRY R. BROWN

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National Water-Quality Assessment Program

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- ¥ Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.

- ¥ Describe how water quality is changing over time.

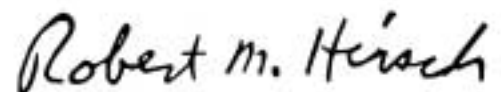
- ¥ Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.



Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS, VERTICAL DATUM, WATER-QUALITY UNITS AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
cubic meter per second (m ³ /s)	35.31	cubic foot per second
gram (g)	0.03527	ounce, avoirdupois
hectare (ha)	0.003861	square mile
kilometer (km)	0.6214	mile
meter (m)	3.281	foot
meter per second (m/s)	3.281	foot per second
millimeter (mm)	0.03937	inch
square kilometer (km ²)	0.3861	square mile

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=1.8^{\circ}\text{C}+32.$$

VERTICAL DATUM

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

WATER-QUALITY UNITS

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

ABBREVIATIONS

$\mu\text{g}/\text{kg}$	microgram per kilogram
μL	microliter
g/kg	gram per kilogram
mL	milliliter

Concentrations of Chlorinated Organic Compounds in Biota and Bed Sediment in Streams of the Lower San Joaquin River Drainage, California

By Larry R. Brown

Abstract

Samples of resident biota and bed sediments were collected in 1992 from 18 sites on or near the floor of the San Joaquin Valley, California, for analysis of 33 organochlorine compounds. The sites were divided into five groups on the basis of physiographic region and land use. Ten compounds were detected in tissue, and 16 compounds were detected in bed sediment. The most frequently detected compound in both media was *p,p'*-DDE. Concentrations of Σ DDT (sum of *o,p'*- and *p,p'*- forms of DDD, DDE, and DDT) were statistically different among groups of sites for tissue and sediment (Kruskal-Wallis, $P < 0.05$). Concentrations in both media were highest in streams draining the west side of the valley. Concentrations of Σ DDT in tissue were significantly correlated with specific conductance, pH, and total alkalinity ($P < 0.05$), which are indicators of the proportion of irrigation-return flows in stream discharge. Concentrations in sediment on a dry-weight basis were not correlated with these water-quality parameters, but total-organic-carbon (TOC) normalized concentrations were significantly correlated with specific conductance and pH ($P < 0.05$). Regressions of the concentration of Σ DDT in tissue as a function of Σ DDT in bed sediment were significant and explained as much as 76 percent of the variance in the data. The concentration of Σ DDT in sediment may be related to mechanisms of soil transport to surface water with bioavailability of compounds related to the concentration of TOC in sediment.

The results of this study did not indicate any clear advantage to using either bed sediment or tissues in studies of organochlorine chemicals in

the environment. Some guidelines for protection of fish and wildlife were exceeded. Concentrations of organochlorine chemicals in biota, and perhaps sediment, have decreased from concentrations measured in the 1970s and 1980s, but remain high compared to other regions of the United States.

INTRODUCTION

The San Joaquin and Tulare Basins, California, encompass about 7.4 million hectares of land and include about 4 million hectares of irrigated agricultural land on the San Joaquin Valley floor. Pesticide use on these agricultural lands is intense in both quantity and variety of chemicals applied. In 1988, a total of 350 pesticides were used and more than 24 million kg of restricted-use pesticides were applied (California Department of Pesticide Regulation, 1988). The potential effects of these chemicals on the health of fish, wildlife, and humans have been a continuing concern (Rasmussen and Blethrow, 1990; Saiki and Schmitt, 1986). This study was undertaken as part of the National Water-Quality Assessment (NAWQA) program of the U.S. Geological Survey (USGS). The overall purpose of the NAWQA program is to describe the status and trends in the quality of the Nation's surface- and ground-water resources and to provide a sound understanding of the natural and human factors that affect the quality of those resources (Leahy and others, 1990). The broad goal of this study was to identify the organochlorine chemicals present in the biota and sediments of the San Joaquin and Tulare basins streams, determine the spatial distribution of those chemicals, and relate the occurrence and distribution of those chemicals to physiographic and land-use characteristics.

Pesticides vary in their potential to affect water quality and the health of organisms, resulting in a wide array of guidelines and standards for resource protection (Nowell and Resek, 1994). Many of the recently developed pesticides, such as the organophosphate compounds, are highly soluble in water and relatively short-lived in the environment. Some organochlorine compounds, however, are poorly soluble in water, and their residues may persist in soil, aquatic sediments, and organisms for long periods of time. Bioaccumulation of these poorly water-soluble compounds in organisms can adversely affect organism health. Recent studies suggest that endocrine disruption also may be adversely affecting organism health because biologically significant effects can result from low concentrations of chemicals in wildlife and humans (Fox, 1992; Leatherland, 1992; Reijnders and Brasseur, 1992; Thomas and Colborn, 1992).

Agricultural use of organochlorine chemicals has been largely eliminated since the early 1970s (Gilliom and others, 1985); however, high concentrations of organochlorine residues have persisted in the sediments (Gilliom and Clifton, 1990) and fish (Saiki and Schmitt, 1986; Rasmussen and Blethrow, 1990, 1991) of San Joaquin Valley streams. In 1981, two samples of carp, *Cyprinus carpio*, collected from the San Joaquin River had total DDT concentrations (the sum of DDD, DDE, and DDT, herein referred to as Σ DDT) of 1,300 and 2,200 $\mu\text{g}/\text{kg}$ wet weight (Saiki and Schmitt, 1986). Both samples exceeded the recommended safe level for the health of fish-eating wildlife of 1,000 $\mu\text{g}/\text{kg}$ wet weight, set by the National Academy of Sciences and National Academy of Engineering (1973). Saiki and Schmitt (1986) also collected a sample of carp with a toxaphene concentration of 3,100 $\mu\text{g}/\text{kg}$ wet weight, which exceeded the National Academy of Sciences and National Academy of Engineering (1973) recommendation of 100 $\mu\text{g}/\text{kg}$ wet weight. Catfish from the lower San Joaquin River have regularly exceeded National Academy of Sciences and National Academy of Engineering (1973) recommended levels and other California criteria for Σ DDT and toxaphene (Rasmussen and Blethrow, 1990).

Despite the high concentrations of organochlorine chemicals detected in fish, few studies in the area have attempted to link tissue concentrations with

environmental sources. Rasmussen and Blethrow (1990) suggested that variability in precipitation influenced the amount of contaminated soil that entered the waterways and subsequently became part of the aquatic food chain. However, they had no sediment data for comparison with their tissue data. Gilliom and Clifton (1990) found elevated bed-sediment concentrations in some streams but did not sample biota to determine if organochlorine compounds were bioaccumulating. Saiki and Schmitt (1986) conducted the most geographically extensive study of tissues within a limited time span (July 1981), but sampled fish only from larger streams and did not sample fish from small intermittent streams and agricultural drains entering the San Joaquin River from the west side of the valley, presumably because their target fish species were not present.

This study emphasized asiatic clam, *Corbicula fluminea*, rather than fish for analyses of organochlorine compounds in tissue for several reasons. First, *Corbicula* were known to be widespread in the study area (Eng, 1979; Leland and Scudder, 1990; Rasmussen and Blethrow, 1990). Second, *Corbicula* have been useful biomonitors of a variety of environmental contaminants and environmental stresses in California and elsewhere (Leard and others, 1980; Elder and Matraw, 1984; Foe and Knight, 1987; Pereira and others, 1988; Johns and others, 1988; Leland and Scudder, 1990; Luoma and others, 1990). Finally, *Corbicula* reside in the west-side tributaries. Fish are not a good bioindicator for the west-side tributaries because the streams often become intermittent during the nonirrigation season (Mullen and others, 1993) and do not provide good year-round habitat for large adult fish, even though these waterways can support high numbers of fish when water is present (Brown, 1998). As a result, fish presumably migrate back and forth between the streams and the San Joaquin River.

Within the broad goal of determining the occurrence and distribution of organochlorine chemicals in biota and sediment, this study addressed the following questions:

1. Are certain organochlorine compounds more likely to be detected in biota (tissue) rather than in sediment?

2. How do the results of this study compare to results of previous studies, including studies of spatial distribution in the San Joaquin Valley, trends over time in the San Joaquin Valley, and concentrations of compounds obtained from national studies?

3. What factors are influencing the concentrations of organochlorine compounds in bed sediment and biota?

4. Do the concentrations of organochlorine compounds found in the study area exceed levels of concern for fish, wildlife, and other aquatic biota?

STUDY AREA

Eighteen collection sites were established on or near the San Joaquin Valley floor (fig. 1, table 1). These sites represented different combinations of land use, physiographic region, and geology (JoAnn Gronberg, U.S. Geological Survey, personal commun., 1995). Sites from similar regions were grouped for analysis. One site on the upper Tuolumne River and one site on the upper Kings River were chosen to represent water-quality conditions in the east-side

Table 1. Sites sampled, site codes, stream discharge, and water-quality data from streams of the San Joaquin Valley, California, October 1992

[Location of sites shown in figure 1. m³/s, cubic meter per second; °C, degree Celsius; µS/cm, microseimen per centimeter at 25 degrees Celsius; mg/L, milligram per liter; --, no data]

Site name	Site code	Discharge (m ³ /s)	Temperature, water (°C)	Specific conductance (µS/cm)	pH	Alkalinity, total (mg/L as CaCO ₃)
Reference sites						
Kings River below Pine Flat Reservoir	REF1	2.24	19.0	55	6.9	23
Tuolumne River at Old La Grange Bridge	REF2	.71	16.5	40	6.8	14
East-side tributaries						
Kings River at People's Weir	ES1	¹ 0	21.0	123	7.6	49
Kings River at Empire weir #2	ES2	¹ 0	19.5	2,630	8.0	297
Merced River near Stevinson	ES3	.91	23.5	324	8.3	--
Tuolumne River at Modesto	ES4	2.83	19.5	320	7.8	96
Dry Creek in Modesto	ES5	.47	19.0	215	7.0	51
Turlock Irrigation District lateral No. 5	ES6	1.02	19.0	422	7.4	118
Stanislaus River near Ripon	ES7	6.12	18.5	94	7.4	44
Mokelumne River near Woodbridge	ES8	.93	19.5	43	7.0	21
West-side tributaries						
Orestimba Creek at River Road	WS1	0.01	21.5	1,260	8.0	206
Spanish Grant Drain	WS2	.14	16.0	1,257	9.4	22
Del Puerto Creek at Vineyard Road	WS3	.12	17.0	783	8.2	96
Salt and Mud Sloughs						
Salt Slough near Stevinson	MS1	0.91	17.5	2,040	7.9	200
Mud Slough near Gustine	MS2	.70	22.0	1,170	8.7	126
San Joaquin River						
San Joaquin River near Stevinson	SJ1	¹ 0	18.5	3,590	8.7	476
San Joaquin River near Patterson	SJ2	² 5.49	18.5	1,636	7.6	214
San Joaquin River near Vernalis	SJ3	15.58	21.0	848	7.9	133

¹ Water was pooled at these locations at the time of sampling.

² Data from California Department of Water Resources.

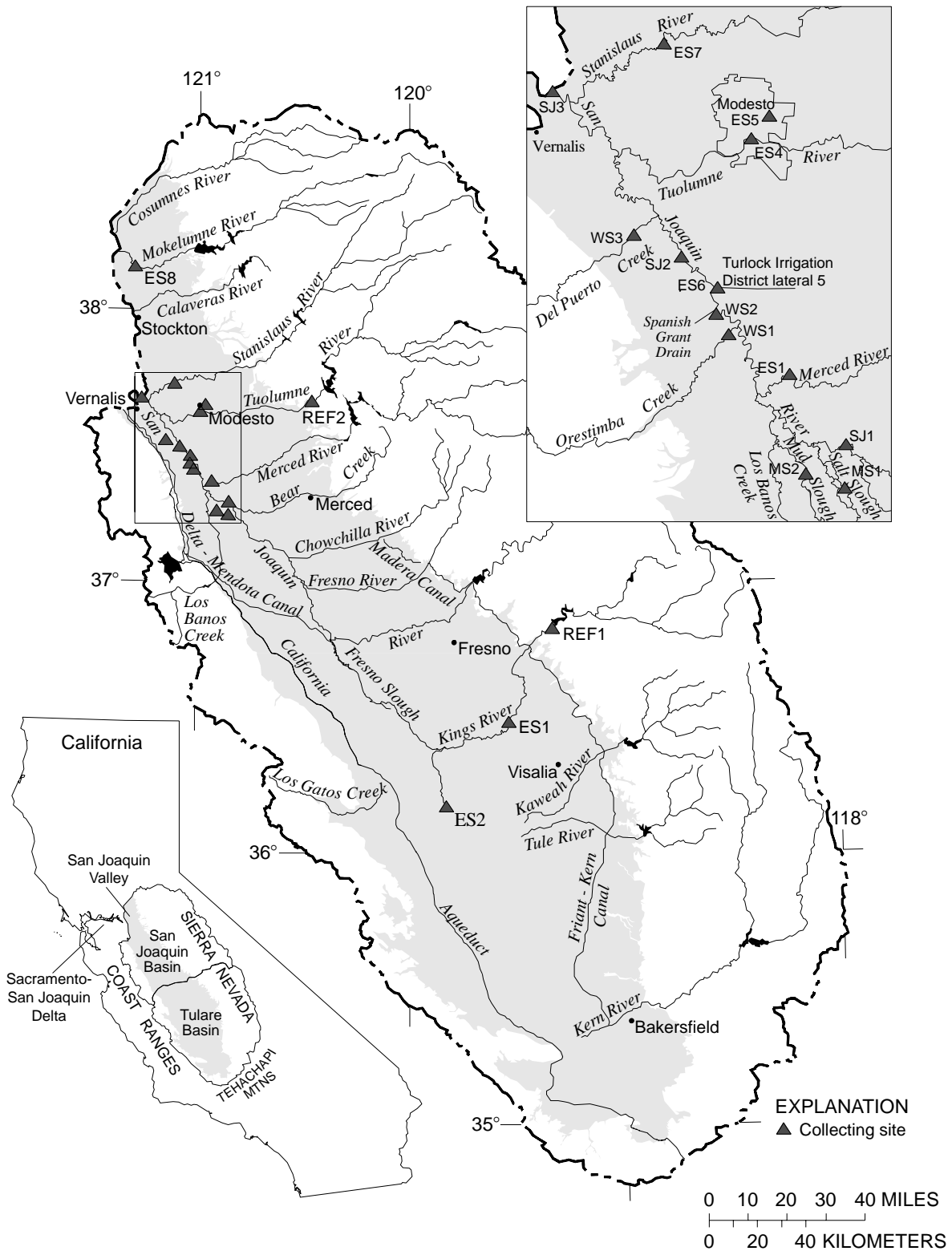


Figure 1. Locations of sample sites in the San Joaquin River drainage, California. Refer to table 1 for full site names.

tributaries, the large, perennial tributaries draining the eastern side of the San Joaquin Valley before the rivers flowed through urban and agricultural areas (reference sites). These sites were located downstream of large reservoirs near the transition from the foothill ecoregion to the Central Valley ecoregion (Omernik, 1987). Land uses in these drainage basins, upstream of the sites, are primarily forest and rangeland with little irrigated agriculture.

Eight sites were selected to represent the east-side streams of the San Joaquin Valley (east-side tributary sites) (table 1). One site each was on the Merced, Tuolumne, Stanislaus, and the Mokelumne Rivers. Two sites were on the lower Kings River. Another site was on Dry Creek, a tributary to the Tuolumne River. The final site was on Turlock irrigation lateral No. 5, a canal that discharges directly into the San Joaquin River. The east side of the valley is characterized by coarse, permeable soils derived from the Sierra Nevada. Land use between these sites and the reference sites includes primarily orchards and vineyards.

Three sites were selected to represent conditions in the waterways of the northern part of the west side of the San Joaquin Valley (west-side tributary sites) (table 1). One site each was on Orestimba Creek, Spanish Grant Drain, and Del Puerto Creek. This area is characterized by fine, relatively impermeable soils derived from the Coast Ranges. Land use upstream of the sites is primarily orchards, row crops, and field crops.

Two sites were selected to represent conditions in the sloughs south of the west-side tributaries (Salt and Mud Sloughs sites) (table 1). This area, known as the "Grasslands," is somewhat unique. The sloughs drain a flood basin that includes the most extensive wetland area remaining in the San Joaquin Valley and also large areas of cropland. One site each was on Salt and Mud Sloughs. Land use is mixed agriculture, grazing, and seasonal wetlands. The dominant crop is cotton.

Three sites were on the San Joaquin River (San Joaquin River sites) (table 1). The first was above the majority of agricultural return flow to the river. The second was between the confluences of the Merced and Tuolumne Rivers. The third was below the inputs of the remaining streams sampled, except the Mokelumne River, which flows directly into the Sacramento-San

Joaquin Delta and the Kings River sites in the hydrologically closed Tulare Basin. In addition to the sampled waterways, many other drains, wasteways, and small streams discharge into the San Joaquin River. The most downstream San Joaquin River site, in essence, integrates the effects of all upstream inputs.

METHODS AND MATERIALS

Sediment samples were collected in October 1992, and tissue samples were collected in October and November 1992. Water temperature was determined to the nearest 0.5°C using an electronic thermometer. Specific conductance and pH were determined with electronic meters. Alkalinity was determined by titration. At gaged sites, discharge was determined from USGS or California Department of Water Resources records as the daily discharge on the day of sampling. An instantaneous discharge measurement was taken at ungaged sites. TOC content of sediment was determined as the difference between total carbon and carbonate (inorganic) carbon by the USGS National Water Quality Laboratory in Arvada, Colo. Percent silt (<63 µm) was determined by sieve analysis at the California District Sediment Laboratory in Salinas, Calif.

Sample Collection

Tissue samples were collected and processed using a variety of techniques (Crawford and Luoma, 1993). Samples of *Corbicula* were collected with stainless steel clam rakes, nylon dip nets, or by hand. Clams were measured (maximum shell width in mm) with stainless steel or plastic calipers and placed in native water in stainless steel pans. The pans were placed in an ice chest cooled with wet ice, and the clams were allowed to depurate for 24 hours. After depuration, the clams were removed, rinsed in native water, wrapped in aluminum foil, and frozen on dry ice.

Fish and crayfish were collected with seines. Fish were measured (standard length, SL) and weighed (grams). The fish then were dissected to determine their sex. A composite sample of seven or eight fish was wrapped in aluminum foil and frozen on dry ice. Crayfish also were depurated for 24 hours. The sex of

the crayfish was determined, and their claws were removed. A composite sample of seven was wrapped in aluminum foil and frozen on dry ice. All tissue samples remained frozen until analysis. Latex or poly-vinyl-chloride gloves were worn during all collecting and processing activities.

Sediment samples were collected from near-shore, depositional areas using a Teflon coring tube, Teflon-coated spoon, or Teflon spatula (Shelton and Capel, 1994). Sampling focused on the upper 2 cm of recently deposited fine sediments. Multiple samples were taken from one to five depositional areas, depending on availability of fine sediments. The material was composited in a glass bowl and thoroughly mixed. About 400 mL of sediment were wet sieved through a 2-mm stainless steel screen into a precleaned glass jar. The sample then was frozen on dry ice and kept frozen until analysis. All stainless steel and Teflon equipment was thoroughly washed, rinsed with methanol, and air dried before use. A separate sample was taken from the composite for determination of percentages of sand and silt (silt defined as particles <63 μm). Latex or poly-vinyl-chloride gloves were worn during all collection and processing activities.

Tissue Analysis

Analyses of the samples were done at the USGS National Water-Quality Laboratory in Arvada, Colorado. Methods are described in detail by Leiker and others (1995). Briefly, all clams in a sample were thawed, and the soft tissues removed from the shell. The soft tissue was homogenized with a blender; fish and crayfish were homogenized whole. A 10 g aliquot of the homogenized tissue was removed and mixed with 100 g of granular, anhydrous sodium sulfate and Soxhlet extracted overnight with methylene chloride. After extraction, the extract was concentrated to a volume of 5 mL, and a 1-mL aliquot was removed for determination of the lipid content. A 2-mL aliquot then was injected into an automated gel permeation chromatograph (GPC) to separate the lipid material and other interferences from the method compounds. After the compounds were collected from the GPC, the extract was solvent exchanged into hexane and

separated into two fractions on a column packed from top to bottom with 1 cm of sodium sulfate, 5 g of 8.5 percent water deactivated alumina, 3 g of 2 percent water deactivated silica, and 0.5 cm of sodium sulfate. The first fraction contained the PCBs, DDE, and other nonpolar organics. The second fraction contained toxaphene, chlordane components, DDT, DDD, and other more polar organic compounds. Each fraction was concentrated to a volume of 1 mL and analyzed by dual capillary-column gas chromatography (GC) with electron-capture detection (Leiker and others, 1995).

Sediment Analysis

Methods for sediment analysis are described in detail in Foreman and others (1995). In summary, frozen sediment was thawed and centrifuged to remove excess water. The centrifuged sample was thoroughly homogenized, and an approximately 2-g aliquot was placed on a drying balance for determination of dry weight. A sample equivalent to 25 g of sediment on a dry-weight basis was mixed with sodium sulfate to remove residual water and Soxhlet extracted overnight with dichloromethane. After extraction, the extract then was concentrated to a volume of about 2 mL. The sample extract was centrifuged, filtered through a 0.2- μm polytetrafluoroethylene syringe filter, and brought up to 3 mL with dichloromethane. An 800- μL aliquot was injected into a GPC system to remove unwanted high molecular-weight natural-organic matter and inorganic sulfur. The GPC fraction was solvent exchanged into hexane and separated into two fractions on a column packed from top to bottom with 1 cm of sodium sulfate, 5 g of 8.5 percent water deactivated alumina, 3 g of 2 percent water deactivated silica, and 1 cm of sodium sulfate. The fractions were concentrated to about 0.5 mL and analyzed by dual capillary-column GC with electron-capture detection. Compound recognition and quantitation procedures were the same as those for tissue.

The minimum reporting limits for the compounds analyzed in this study ranged from 1 to 100 $\mu\text{g}/\text{kg}$ (table 2). The reporting limit for most compounds was lower in sediment than in tissue. In some cases, reporting limits were higher due to chemical interferences unique to the sample. Quality

assurance included duplicate field collections of sediment, laboratory analyses of replicates, blanks, reagent spikes, and surrogates added to each environmental sample and reagent spike. Tissue surrogates (and mean recoveries) were alpha-HCH-d6 (92 percent) and 3,5-decachlorobiphenyl (82 percent). Sediment surrogates were alpha-HCH-d6 (75 percent), 3,5-decachlorobiphenyl (55 percent), and 2,2',3,4',5,6,6'-octachlorobiphenyl (63 percent). No adjustments for recovery efficiency were made.

Data Analysis

Shell widths of *Corbicula* and standard lengths of carp were log-transformed for analysis of variance (ANOVA). Untransformed data were analyzed using nonparametric statistical procedures, including Spearman rank correlations and Kruskal-Wallis comparisons among groups of sites (table 1). Normalization of tissue data by lipid content and sediment data by TOC content are discussed in the results. The only organochlorine constituents common enough for statistical analysis were the DDT group of compounds; analyses were done on Σ DDT only. When the concentration of any component was determined to be less than the reporting limit, a value of one-half the limit was added to the total for statistical tests only. Values given in the text and tables assume a value of zero when the concentration is less than the reporting limit.

The relation between concentrations of Σ DDT in tissue and in sediment was explored using regression analysis. Because a number of taxa were collected during the study, tissue data analyses were done on all taxa combined and *Corbicula*, the most commonly collected organism. The results from each data set then were compared to minimize the possibility of misinterpreting patterns caused by mixing results from different taxa. Concentrations of organochlorine compounds in tissue were compared to National Academy of Sciences and National Academy of Engineering (1973) guidelines for the protection of fish-eating wildlife. Concentrations in sediment were compared to U.S. Environmental Protection Agency (1988) interim guidelines and draft Canadian guidelines (Environment Canada, 1995) for protection of aquatic organisms.

Table 2. Minimum reporting limits for organochlorine compounds analyzed in tissue and sediment collected from San Joaquin Valley streams, California, October 1992

[Chemical numbers as listed in Chemical Abstracts. NA, analysis not conducted in this medium. $\mu\text{g}/\text{kg}$, microgram per kilogram; --, not applicable]

Compound	Chemical abstract number	Reporting limit ($\mu\text{g}/\text{kg}$)	
		Sediment (dry weight)	Tissue (wet weight)
Aldrin.....	309-00-2	¹ 1.0	¹ 5.0
<i>cis</i> -Chlordane.....	5103-71-9	1.0	¹ 5.0
<i>trans</i> -Chlordane.....	5103-71-9	1.0	¹ 5.0
Chloroneb.....	2675-77-6	¹ 5.0	NA
Dacthal ²	1861-32-1	5.0	5.0
<i>o,p</i> \leftarrow -DDD.....	53-19-0	1.0	5.0
<i>p,p</i> \leftarrow -DDD.....	72-54-8	1.0	5.0
<i>o,p</i> \leftarrow -DDE.....	3424-82-6	1.0	5.0
<i>p,p</i> \leftarrow -DDE.....	72-55-9	1.0	5.0
<i>o,p</i> \leftarrow -DDT.....	789-02-6	2.0	5.0
<i>p,p</i> \leftarrow -DDT.....	50-29-3	2.0	5.0
Dieldrin.....	60-57-1	1.0	5.0
Endosulfan I.....	959-98-9	¹ 1.0	NA
Endrin.....	72-20-8	¹ 2.0	¹ 5.0
α -HCH.....	319-84-6	¹ 1.0	NA
β -HCH.....	319-85-7	¹ 1.0	NA
δ -HCH.....	319-86-8	NA	¹ 5.0
γ -HCH.....	58-89-9	¹ 1.0	¹ 5.0
Heptachlor.....	76-44-8	¹ 1.0	¹ 5.0
Heptachlor epoxide.....	1024-57-3	¹ 1.0	¹ 5.0
Hexachlorobenzene.....	118-74-1	¹ 1.0	¹ 5.0
Isodrin.....	465-73-6	¹ 1.0	NA
<i>o,p</i> \leftarrow -Methoxychlor.....	30667-99-3	¹ 5.0	¹ 5.0
<i>p,p</i> \leftarrow -Methoxychlor.....	72-43-5	¹ 5.0	¹ 5.0
Mirex ³	2385-85-5	¹ 1.0	¹ 5.0
<i>cis</i> -Nonachlor.....	5103-73-1	1.0	¹ 5.0
<i>trans</i> -Nonachlor.....	39765-80-5	1.0	¹ 5.0
Oxychlordane.....	27304-13-8	¹ 1.0	¹ 5.0
PCBs, total.....	--	¹ 100.0	50.0
Pentachloranisole.....	1825-21-4	¹ 1.0	¹ 5.0
<i>cis</i> -Permethrin.....	61949-76-6	5.0	NA
<i>trans</i> -Permethrin.....	61949-77-7	5.0	NA
Toxaphene.....	8001-35-2	100.0	100.0

¹Constituents never detected in this study.

²1,1a,2,2,3,3a,4,5,5,5a,5b,6-dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta(cd)pentalene

³ DCPA; dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate

RESULTS

Mean size of clams varied significantly among sample sites (ANOVA, $F_{11,1365} = 208.8$, $P < 0.001$). Sample sizes were large and statistically significant differences were found between sites where mean size of *Corbicula* differed by less than 2 mm (table 3). The lowermost San Joaquin River site (SJ3) (fig. 1) had the largest mean size of 44 mm; mean size of clams at the other sites ranged from 18 to 28 mm. Mean length of carp in a composite sample also varied among sample sites (table 3, ANOVA, $F_{2,19} = 26.4$, $P < 0.0001$). Each of the sites were statistically different from the others (Tukey's HSD, $P < 0.05$).

Table 3. Number, mean size, standard deviation and percent lipid of organisms in composite samples collected from each sample site, San Joaquin River drainage, October 1992

[Mean size is shell width for *Corbicula*, standard length for fish, and total length from anterior tip of carapace to end of tail for crayfish. Within a species, means that were not significantly different based on Tukeys HSD ($P > 0.05$) are indicated by similar subscripts. Sites with *Corbicula* are presented in order of decreasing mean width]

Site code	Number	Mean (mm)	Standard deviation (mm)	Lipid (percent)
<i>Corbicula</i>				
SJ3	28	44 _a	8	1.90
WS2	64	28 _b	8	2.80
REF2	100	28 _{b,c}	2	1.00
ES4	100	26 _{c,d}	2	2.90
ES1	151	25 _d	1	1.40
ES3	110	25 _{d,e}	1	2.60
ES7	100	23 _{e,f}	4	2.80
ES5	123	23 _{e,f}	2	0.70
REF1	140	23 _f	2	1.30
WS3	116	20 _g	6	0.74
WS1	145	19 _{g,h}	3	1.36
ES8	200	18 _h	2	0.90
Carp				
ES2	7	201 _a	64	3.0
MS2	8	107 _b	15	3.6
SJ2	7	238 _c	34	2.2
Channel catfish				
MS1	7	112	39	3.3
Bluegill				
SJ1	7	102	13	3.4
Crayfish				
ES6	7	79	8	3.0

There was no correlation between mean width and lipid content of clams in composite samples ($r_s = 0.51$, $df = 10$, $P > 0.05$); however, lipid content of *Corbicula* tended to be lower than that of other organisms (table 3). Neither was there any statistical difference among regions in lipid content for either the full data set (Kruskal-Wallis, $H = 7.0$, $df = 4$, $P > 0.05$) or *Corbicula* only (Kruskal-Wallis, $H = 1.0$, $df = 3$, $P > 0.05$). There was also no correlation between lipid content and concentration of Σ DDT for either the full data set ($r_s = 0.35$, $df = 16$, $P > 0.05$) or *Corbicula* only ($r_s = 0.31$, $df = 10$, $P > 0.05$). Based on these results, neither data set was normalized for lipid content because there did not appear to be any relation between lipid content and Σ DDT concentration in tissue.

Table 4. Total organic carbon content and percent silt (< 63 μ m) in sediment from each sample site by region, San Joaquin River drainage, October 1992

[Results from duplicate samples appear in parentheses. Total organic carbon content is in grams of carbon per kilogram of sediment, dry weight. --, no data]

Site code	Total organic carbon content	Percent silt (percentage of dry weight)
Reference sites		
REF1	44.0	43
REF2	11.6	6
East-side tributaries		
ES1	--	--
ES2	4.0	16
ES3	11.0	14
ES4	9.2	15
ES5	9.0	16
ES6	18.0	26
ES7	9.5	17
ES8	15.0	33
West-side tributaries		
WS1	7.4(5.8)	56(60)
WS2	8.3(8.4)	63
WS3	8.5	44
Salt and Mud Sloughs		
MS1	6.6(9.2)	27(39)
MS2	7.2	35
San Joaquin River		
SJ1	6.7	14
SJ2	2.0	15
SJ3	5.2	32

Sediment characteristics also varied among sites (table 4). Percent silt ranged from 6 to 63 percent of sediment dry weight, and TOC content ranged from 2.0 to 44.0 g/kg sediment dry weight. No correlation between percent silt and TOC content of sediments ($r_s = 0.01$, $df = 15$, $P > 0.05$) was found.

Concentrations of Σ DDT in sediment ($\mu\text{g}/\text{kg}$ dry weight) were positively correlated with percent silt ($r_s = 0.57$, $df = 15$, $P < 0.05$), but were not correlated with TOC ($r_s = -0.03$, $df = 15$, $P > 0.05$). Although there was no statistically significant difference among regions for percent silt (Kruskal-Wallis, $H = 8.6$, $df = 4$, $P > 0.05$), statistically significant differences for TOC existed among regions (Kruskal-Wallis, $H = 10.4$, $df = 4$, $P < 0.05$). Median TOC concentrations for dry sediment decreased from 27.8 g/kg at the reference sites to 9.5 g/kg at east-side sites, 8.3 g/kg at the west-side sites, 6.9 g/kg at Mud and Salt Sloughs, and 5.2 g/kg at the San Joaquin River sites. A sediment sample was not collected at the Kings River site (ES1) (fig. 1) because most of the sediment had recently dried, and the sediment in the pools containing *Corbicula* had been disturbed. Because of the differences in TOC content in sediment among regions and the significant correlation between silt and Σ DDT, data sets normalized by TOC and silt were analyzed and compared to results obtained with nonnormalized data.

A total of 16 compounds were detected, 10 compounds in tissue and 15 compounds in sediment (table 5). Sixteen of the 26 constituents analyzed in tissue and 17 of the 32 constituents analyzed in sediment were never detected (table 2). Of the constituents found in both media, the most frequently detected was *p,p'*-DDE (fig. 2). The frequency of occurrence for compounds found in both media tended to be similar in tissue and sediment (fig. 2). PCBs were detected only in tissue (2 sites), and *cis*-nonachlor, *trans*-nonachlor, *cis*-permethrin, *trans*-permethrin (all at 1 site), and *o,p'*-DDD (3 sites) were detected only in sediment. The number of compounds detected at a particular site ranged from 0 to 9 in tissue (fig. 3A) and from 0 to 10 in sediment (fig. 3B). Constituents were not detected in the biota or sediment collected from the reference sites (table 5). The only constituent detected in the biota collected at east-side sites was *p,p'*-DDE, except for one site where *p,p'*-DDT also was detected.

Concentrations of Σ DDT varied among regions for both media (table 5). The concentrations of Σ DDT in tissue generally were highest at the west-side sites (fig. 4; table 5). There were significant differences among regions for the total data set (Kruskal-Wallis, $H = 14.0$, $df = 4$, $P < 0.05$) and the *Corbicula* data set (Kruskal-Wallis, $H = 9.5$, $df = 3$, $P < 0.05$). Concentrations of Σ DDT in sediment also were highest at west-side sites (fig. 5; table 5).

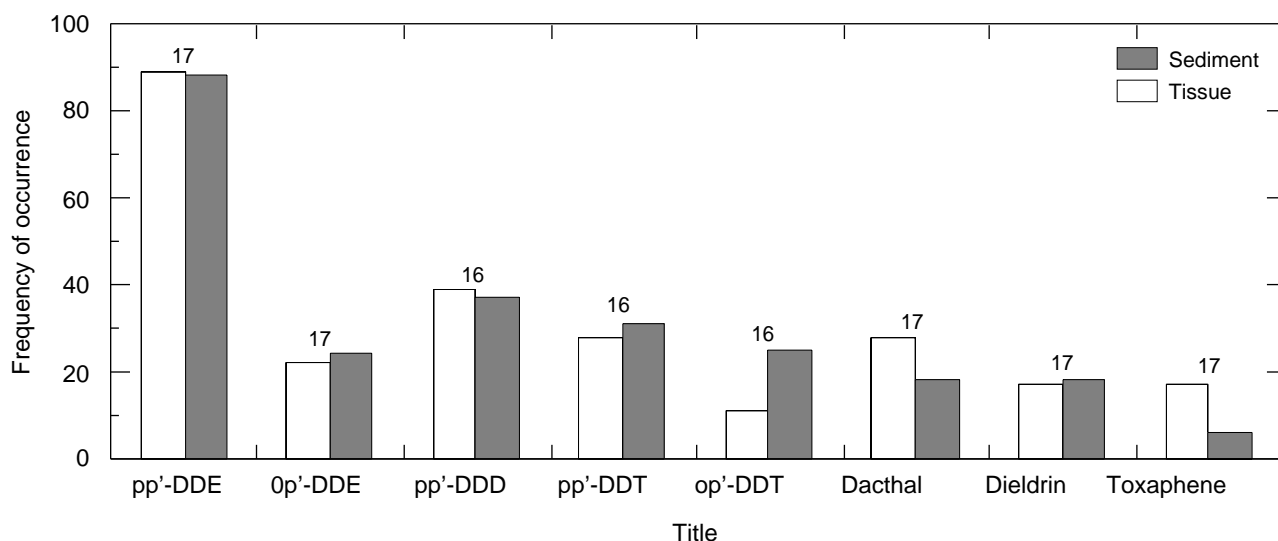


Figure 2. Frequency of occurrence (percentage) for compounds detected in both tissue and sediment. Number of sites where data are available is shown for sediment. Number of sites for tissue was 18.

Table 5. Concentrations of organochlorine compounds in tissue of biota and sediment from streams of the San Joaquin Valley, California, October 1992

[Site code: Concentrations for duplicate sediment samples are tabulated under the appropriate site code appended with a D. **Organochlorine compounds:** Concentrations of Σ DDT assume a concentration of 0 when a compound was not detected. For statistical tests, a concentration of one-half of the reporting limit was used. M, analyte broke down into other DDT compounds during injection. Concentrations were reported by the laboratory as the sum of *p,p'*-DDX or *o,p'*-DDX compounds. NA, not analyzed in this media; dw, dry weight; ww, wet weight; U, analyte deleted due to interferences. --, no data]

Site code	Organochlorine compounds in micrograms per kilogram													
	<i>cis</i> -Chlor-dane		<i>trans</i> -Chlor-dane		Dacthal®		<i>o,p'</i> -DDD		<i>p,p'</i> -D		<i>o,p'</i> -DDE		<i>p,p'</i> -DDE	
	ww	dw	ww	dw	ww	dw	ww	dw	ww	dw	ww	dw	ww	dw
REF1	<5	<1	<5	<1	<5	<5	<5	<1	<5	<1	<5	<1	<5	<1
REF2	<5	<1	<5	<1	<5	<5	<5	<1	<5	<1	<5	<1	<5	<1
ES1	<5	--	<5	--	<5	--	<5	--	<5	--	<5	--	16	--
ES2	<5	<1	<5	<1	<5	<5	<5	<1	5.7	<1	<5	<1	95	<1
ES3	<5	<1	<5	<1	<5	<5	<5	<1	<5	<1	<5	<1	22	1.6
ES4	<5	<1	<5	<1	<5	¹ <5	<5	1.0	<5	4.0	<5	<1	14	31
ES5	<5	<1	<5	<1	<5	<5	<5	<1	<5	<1	<5	<1	11	2.3
ES6	<5	<1	<5	<1	<5	<5	<5	<1	<5	<1	<5	1	6.3	3.7
ES7	<5	<1	<5	<1	<5	<5	<5	M	<5	M	<5	<1	6.1	1.5
ES8	<5	2.1	<5	2.3	<5	<5	<5	<1	<5	<1	<5	<1	5.8	3.5
MS1	<5	<1	<5	<1	<5	<5	<5	<1	22	1.2	<5	<1	320	3.3
MS1D	--	<1	--	<1	--	<5	--	<1	--	1.4	--	<1	--	5.7
MS2	<5	<1	<5	<1	<5	<5	<5	<1	9.8	<1	<5	<1	69.5	1.4
SJ1	<5	<1	<5	<1	<5	<5	<5	<1	<5	<1	<5	<1	50	<1
SJ2	<5	<1	<5	<1	23	<5	<5	<1	24	<1	<5	<1	480	1.0
SJ3	<5	<1	<5	<1	33	<5	<9	<1	18	2.9	5.4	<1	240	7.9
WS1	<5	U	<5	U	270	32	20.0	15	100	39	22	11	1,100	240
WS1D	--	<1	--	<1	--	25	--	4.9	--	38	--	4.4	--	174
WS2	<5	<1	<5	<1	360	<7	<37	<1	<40	11	12	1.8	1,600	80
WS2D	--	<1	--	<1	--	5	--	M	--	M	--	1.9	--	87
WS3	<5	<1	<5	<1	11	¹ <5	7.4	1.7	27	10	14	2.3	350	69

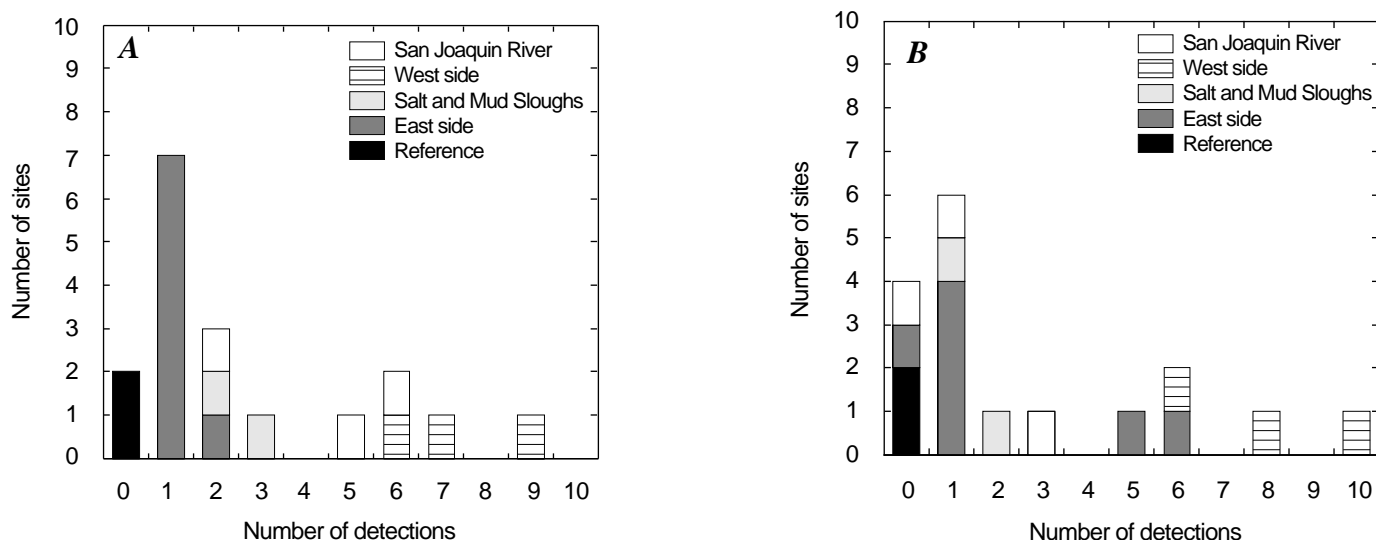


Figure 3. Number of compounds detected at each site in (A) tissue and (B) sediment.

Table 5. Concentrations of organochlorine compounds in tissue of biota and sediment from streams of the San Joaquin Valley, California, October 1992. *Continued*

Site code	Organochlorine compounds, in micrograms per kilogram											
	o,p'-DDT		p,p'-DDT		ΣDDT		Dieldrin		cis-Nonachlor		trans-Nonachlor	
	ww	dw	ww	dw	ww	dw	ww	dw	ww	dw	ww	dw
REF1	<5	<2	<5	<2	0	0	<5	<1	<5	<1	<5	<1
REF2	<5	<2	<5	<2	0	0	<5	<1	<5	<1	<5	<1
ES1	<5	--	<5	--	16	--	<5	--	<5	<1	<5	<1
ES2	<5	<2	<5	<2	101	.0	<5	<1	<5	<1	<5	<1
ES3	<5	<2	<5	<2	22	1.6	<5	<1	<5	<1	<5	<1
ES4	<5	¹ <2	<5	13.5	14	50	<5	<1	<5	<1	<5	<1
ES5	<5	<2	<5	<2	11	2.3	<5	<1	<5	<1	<5	<1
ES6	<5	<2	<5	<2	6.3	4.7	<5	<1	<5	<1	<5	<1
ES7	<5	M	<5	M	6.1	1.5	<5	<1	<5	<1	<5	<1
ES8	<5	<2	<5	<2	5.8	3.5	<5	<1	<5	1.5	<5	2.3
MS1	<5	<2	<5	<2	342	4.5	5.9	<1	<5	<1	<5	<1
MS1D	--	<2	--	<2	--	7.1	--	<1	--	<1	--	<1
MS2	<5	<2	<5	<2	79.3	1.4	<5	<1	<5	<1	<5	<1
SJ1	<5	<2	<5	<2	50	.0	5.5	<1	<5	<1	<5	<1
SJ2	<5	<2	5.9	<2	510	1.0	<5	<1	<5	<1	<5	<1
SJ3	<9	<2	32	2.4	295	13	<5	<1	<5	<1	<5	<1
WS1	36	42	220	68	1,498	415	9.8	9.7	<5	U	<5	U
WS1D	--	30	--	51	--	302	--	3.5	--	<1	--	<1
WS2	<5	3.2	580	13	2,192	109	<35	2.5	<5	<1	<5	<1
WS2D	--	M	--	M	--	110	--	1.3	--	<1	--	<1
WS3	18	3.9	93	33	509	120	<5	1.0	<5	<1	<5	<1

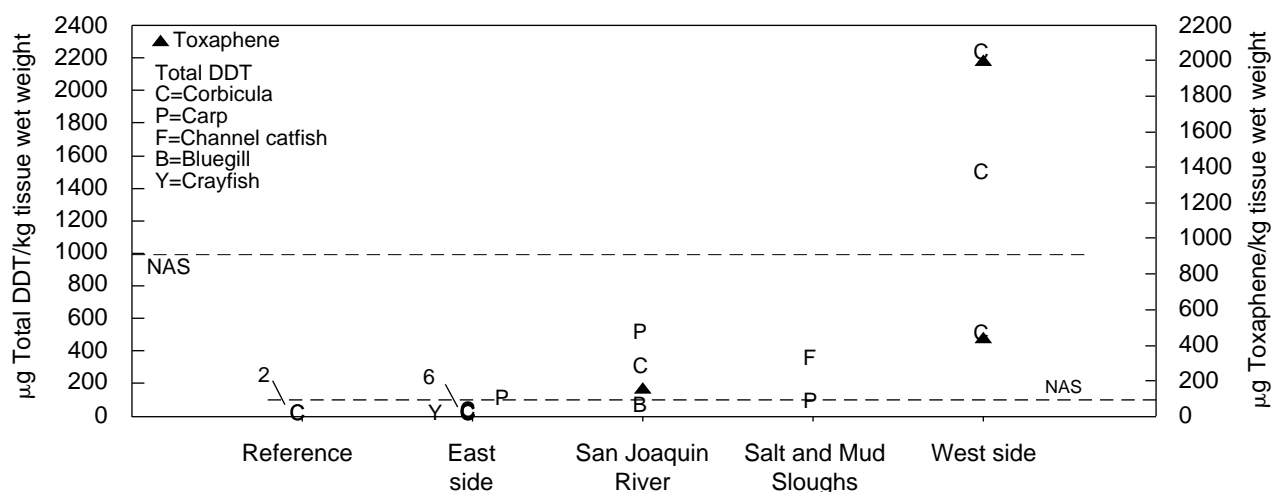


Figure 4. Concentrations of ΣDDT and toxaphene (all *Corbicula* samples) in tissue compared to National Academy of Science, National Academy of Engineering (NAS) guideline for protection of fish eating wildlife (National Academy of Sciences and National Academy of Engineering, 1973).

Table 5. Concentrations of organochlorine compounds in tissue of biota and sediment from streams of the San Joaquin Valley in October 1992. *Continued*

Site code	<i>cis</i> -Permethrin		<i>trans</i> -Permethrin		Toxaphene		PCBs	
	ww	dw	ww	dw	ww	dw	ww	dw
REF1	NA	<5	NA	<5	<100	<100	<50	<100
REF2	NA	<5	NA	<5	<100	<100	<50	<100
ES1	NA	--	NA	--	<100	--	<50	--
ES2	NA	<5	NA	<5	<100	<100	<50	<100
ES3	NA	<5	NA	<5	<100	<100	<50	<100
ES4	NA	<5	NA	<5	<100	<100	<50	<100
ES5	NA	<5	NA	<5	<100	<100	<50	<100
ES6	NA	<5	NA	<5	<100	<100	<50	<100
ES7	NA	U	NA	U	<100	<100	<50	<100
ES8	NA	<5	NA	<5	<100	<100	<50	<100
MS1	NA	<5	NA	<5	<100	<100	<50	<100
MS1D	NA	<5	NA	<5	--	<100	--	<100
MS2	NA	<5	NA	<5	<100	<100	<50	<100
SJ1	NA	<5	NA	<5	<100	<100	<50	<100
SJ2	NA	<5	NA	<5	<100	<100	52	<100
SJ3	NA	<5	NA	<5	160	<100	<50	<100
WS1	NA	<5	NA	<5	440	630	<50	<100
WS1D	--	<5	--	<5	NA	240	NA	<100
WS2	NA	<5	NA	<5	2,000	<100	57	<100
WS2D	--	U	--	U	NA	<100	NA	<100
WS3	NA	16	NA	15	<100	<100	<50	<100

¹Analyte was positively identified as present but the concentration was less than the reporting limit and could not be accurately quantified.

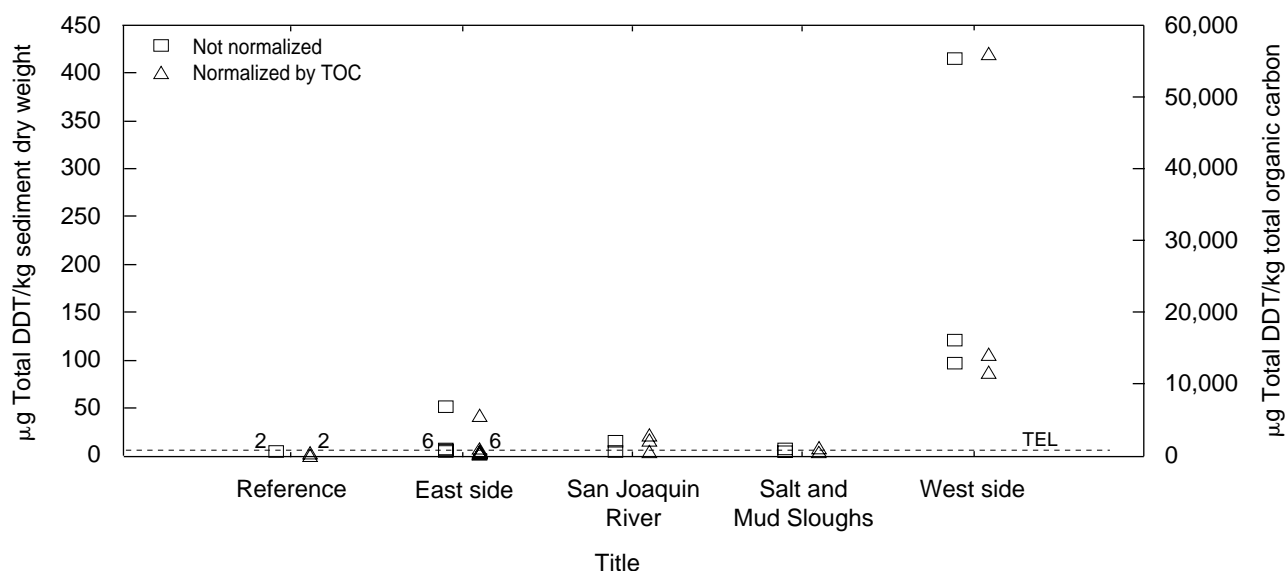


Figure 5. Concentrations of Σ DDT found in sediment on a dry weight basis and normalized by total organic carbon content of sediment. Results are compared to the threshold effect level from the Canadian interim sediment quality guidelines (Environment Canada, 1995).

Normalization of data by TOC did not noticeably reduce the variability within or among regions. The concentrations of Σ DDT in sediment were significantly different among regions for both sediment dry-weight data (Kruskal-Wallis, $H=9.8$, $df=4$, $P<0.05$) and TOC-normalized data (Kruskal-Wallis, $H = 11.5$, $df = 4$, $P<0.05$), but not for silt-normalized data (Kruskal-Wallis, $H=7.2$, $df=4$, $P>0.05$).

The concentrations of several organochlorine compounds found in tissue and sediment during this study are high compared to a number of national standards and guidelines. Concentrations in biota at several west-side and San Joaquin River sites exceeded the National Academy of Sciences and National Academy of Engineering (1973) recommended tissue concentrations for protection of fish-eating wildlife [Σ DDT (1,000 $\mu\text{g}/\text{kg}$ wet weight in whole fish) or for toxaphene (100 $\mu\text{g}/\text{kg}$ wet weight in whole fish)] (fig. 4).

Several sites exceeded EPA-draft sediment criteria for organochlorine compounds. Four sites exceeded the draft criteria (U.S. Environmental Protection Agency, 1988) for p,p' -DDT (828 $\mu\text{g}/\text{kg}$ TOC dry weight) when standardized by TOC: Tuolumne River near Modesto (ES4) (fig. 1), 1,467 $\mu\text{g}/\text{kg}$ TOC dry weight; Orestimba Creek (WS1), 9,189 $\mu\text{g}/\text{kg}$ TOC dry weight; Spanish Grant Drain (WS2), 1,566 $\mu\text{g}/\text{kg}$ TOC dry weight; and Del Puerto Creek (WS3), 3,882 $\mu\text{g}/\text{kg}$ TOC dry weight. The concentrations of toxaphene in the sediment sample and the duplicate from Orestimba Creek (85 and 135 $\mu\text{g}/\text{kg}$ TOC dry weight, respectively) exceeded the draft criteria (U.S. Environmental Protection Agency, 1990) for that compound (64.7 $\mu\text{g}/\text{kg}$ TOC dry weight).

A number of sites also exceeded Canadian interim sediment quality guidelines (Environment Canada, 1995). The Tuolumne River (ES4) exceeded the threshold effect level (the concentration below which adverse effects are expected to occur rarely) for p,p' -DDD (3.54 $\mu\text{g}/\text{kg}$ dry weight) and the three west-side sites (WS1-3) exceeded the probable effect level (the concentration above which adverse effects are predicted to occur frequently) (8.51 $\mu\text{g}/\text{kg}$ dry weight) (table 5). The sites at Merced River (ES3), Dry Creek (ES5), Turlock Irrigation District Lateral 5 (ES6), Stanislaus River (ES7), Mokelumne River (ES8), and Salt Slough (MS1) all exceeded the threshold effect level for p,p' -DDE (1.42 $\mu\text{g}/\text{kg}$ dry weight); Tuolumne River at Modesto (ES4), San Joaquin River near Vernalis (SJ3), and all three west-side sites (WS1-3)

exceeded the probable effect level (6.75 $\mu\text{g}/\text{kg}$ dry weight) (table 5). However, the guidelines for Σ DDT were exceeded less often with only the Tuolumne River at Modesto (ES4); the duplicate from Salt Slough (MS1D), San Joaquin River near Vernalis (SJ3), and all three west-side sites (WS1-3) exceeded the threshold effect level (6.98 $\mu\text{g}/\text{kg}$ dry weight) (table 5, fig. 5). The sample from Orestimba Creek (WS1) also exceeded the probable effect level for dieldrin (6.67 $\mu\text{g}/\text{kg}$ dry weight) (table 5).

Concentrations of Σ DDT in tissue ($\mu\text{g}/\text{kg}$ wet weight) were significantly correlated with specific conductance ($r_s = 0.81$, $df = 16$, $P < 0.01$), pH ($r_s = 0.76$, $df = 16$, $P < 0.01$), and total alkalinity ($r_s = 0.56$, $df = 15$, $P < 0.05$). When only *Corbicula* data were considered, significant correlations were found for specific conductance ($r_s = 0.95$, $df = 10$, $P < 0.01$) and pH ($r_s = 0.93$, $df = 10$, $P < 0.01$). The correlation with total alkalinity was nearly significant ($r_s = 0.59$, $df = 9$, $P = 0.05$). Concentrations of Σ DDT in sediment ($\mu\text{g}/\text{kg}$ dry weight) and silt normalized data were not significantly correlated with any of the water-quality parameters. When concentrations were normalized by TOC, significant correlations were found for specific conductance ($r_s = 0.55$, $df = 15$, $P < 0.05$) and pH ($r_s = 0.55$, $df = 15$, $P < 0.05$).

The concentration of Σ DDT in tissue was related to the concentration of Σ DDT in sediment. A regression of Σ DDT concentrations in tissue ($\mu\text{g}/\text{kg}$ wet weight), as a function of concentration of Σ DDT in sediment ($\mu\text{g}/\text{kg}$ dry weight), was significant but accounted for only a moderate part of the variance ($P < 0.01$, $r^2 = 0.46$). Log-transformation of the data did not improve the fit ($P < 0.01$, $r^2 = 0.44$); however, the TOC normalized sediment data did improve the log-transformed regression ($P < 0.001$, $r^2 = 0.67$, fig. 6). The use of the silt-normalized data in the log-transformed regression resulted in the poorest fit ($P < 0.05$, $r^2 = 0.26$). The *Corbicula* data set produced somewhat different results with most of the improvement in fit from the untransformed regression ($P < 0.05$, $r^2 = 0.45$), a result of log-transformation ($P < 0.001$, $r^2 = 0.74$) rather than TOC normalization ($P < 0.001$, $r^2 = 0.76$, fig. 6). Use of silt-normalized data in the log-transformed regression accounted for about the same amount of variation as when the untransformed data were used ($P < 0.05$, $r^2 = 0.46$). The regression equations obtained with the data set, including all biota, did not differ statistically from the

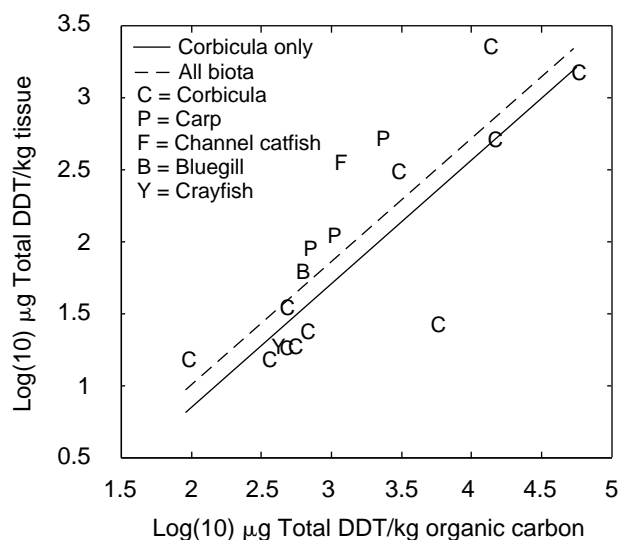


Figure 6. Regressions of \log_{10} of Σ DDT in tissue (wet weight) as a function of \log_{10} of Σ DDT in sediment normalized for total organic carbon. The regression equation for the data set including all biota is: \log_{10} tissue = $0.85(\log_{10}$ TOC-normalized sediment) - 0.69 ($r^2 = 0.67$). The regression using *Corbicula* data only is: \log_{10} tissue = $0.86(\log_{10}$ TOC normalized sediment) - 0.88 ($r^2 = 0.76$).

equations obtained with the *Corbicula* data set for either slope or intercept for any of the sediment data types (analysis of covariance, all $P > 0.05$).

Recalculation of the regressions without the Tuolumne River at Modesto (ES4 in fig. 1 and point in the lower right quadrant of fig. 6), which had a very high concentration of Σ DDT in sediment compared to other east-side sites, improved the proportion of variance explained by the log-transformed regression ($r^2 = 0.56$ for all biota and $r^2 = 0.88$ for *Corbicula*), TOC-normalized regressions ($r^2 = 0.80$ for all biota and $r^2 = 0.90$ for *Corbicula*), and silt-normalized regressions ($r^2 = 0.44$ for all biota and $r^2 = 0.68$ for *Corbicula*). Exclusion of this site did not result in statistically different values for slopes or intercepts for any of the regressions calculated (analysis of covariance, all $P > 0.05$).

DISCUSSION

Relatively few studies have simultaneously assessed concentrations of organochlorine chemicals in sediment and tissue over large geographic areas,

presumably because of cost, specific interest of the researchers, or perceived advantages of one medium over another. Results from this study suggest that unlike tissue, sampling sediment may allow for detection of additional chemicals at low levels. Chlordane and nonachlor were detected only in sediment (table 5). Permethrin also was detected in sediment, but was not one of the compounds analyzed in the tissue method. At individual sites, DDT compounds were sometimes detected in one medium but not the other. Many factors could account for this, including recent deposition of sediments, immigration of organisms, low bioavailability, or differences between detection limits for the two methods. Conversely, toxaphene was detected in tissue at three sites, but only at one site in sediment.

When results from specific sites are compared, it is not clear whether one medium outperforms the other. At two east-side sites (ES4 and ES8) (fig. 1), more compounds were detected in sediment than in tissue, but fewer were detected in sediment at one east-side site (ES2) (table 5). More compounds were detected in tissue than in sediment at all San Joaquin River, Salt Slough, and Mud Slough sites. At west-side sites, the same number of compounds were detected in both media at two sites (WS1 and WS2), and at one site more were detected in sediment (WS3). Overall, DDT compounds, toxaphene, and PCBs were detected more consistently in tissue than in sediment, whereas compounds never or rarely detected in tissue were occasionally detected in sediment.

Other studies suggest that the relative merits of sediment and tissue may depend on the specific situation. Elder and Matraw (1984) detected more constituents in tissue than in either bottom-load detritus or fine-grained sediment. Pereira and others (1994) detected the same group of constituents in both the bottom sediment and in the livers of striped bass (*Morone saxatilis*) collected from San Francisco Bay and the Sacramento-San Joaquin Delta. Pereira and others (1988) found similar numbers of constituents in bottom sediment, suspended sediment, three species of fish, and a crab from a Louisiana estuary. Pereira and others (1996) found more compounds in bottom and suspended sediment than in *Corbicula* using samples collected at the same time as samples collected for this study at Orestimba Creek (WS1), Dry Creek (ES8), and the Mokelumne River (ES5); however, the list of

analytes differed, and detection limits were lower than in this study. One practical advantage to sediment collection is that fine-grained sediment is present in most streams, but a single species of organism may not be common to all sites. For example, *Corbicula* could not be collected at six sites sampled in this study, and other organisms had to be collected instead. However, most standards and guidelines have been formulated for tissues because bioaccumulation of these compounds and their biological effects on biota are the source of concern rather than the presence of organochlorine chemicals in sediment.

The presence of organochlorine pesticides in the biota and sediments of the lower San Joaquin River has been noted in previous studies (Saiki and Schmitt 1986; Gilliom and Clifton 1990; Rasmussen and Blethrow, 1990, 1991). Concentrations in biota have decreased in the east-side tributaries and San Joaquin River, where data were available for comparison. Composite samples of channel catfish filets, collected in 8 of the 10 years during 1978 to 1987 from the San Joaquin River near Vernalis (fig. 1), averaged 2,200 µg/kg wet weight for ΣDDT and 4,500 µg/kg wet weight for toxaphene (Rasmussen and Blethrow 1991). Concentrations in 1988 were similar to those in 1987 for ΣDDT (1,739 µg/kg wet weight), but the concentration of toxaphene was about one-half the 1987 concentration of 620 µg/kg wet weight (Rasmussen and Blethrow, 1991). Compared to samples of *Corbicula* (Rasmussen and Blethrow, 1990) and carp (Saiki and Schmitt, 1986), concentrations of

ΣDDT in tissue collected in this study were lower than the previously measured values in 12 of 13 comparisons (table 6).

Though concentrations decreased from those concentrations measured in the 1970s and 1980s, the distribution pattern of high concentrations was similar to past studies. Rasmussen and Blethrow (1990) found that concentrations of organochlorine chemicals in fish tissue from east-side tributaries were sometimes as high as the concentrations measured at the lowest San Joaquin River site (SJ3) (fig. 1), but generally were lower. All tissue samples from east-side tributaries sampled in this study had lower concentrations of organochlorine compounds than samples collected from the San Joaquin River near Vernalis (SJ3). Saiki and Schmitt (1986) also found high concentrations of organochlorine compounds in fish and noted that concentrations generally were lowest at upstream San Joaquin River sites and higher at downstream San Joaquin River sites. Saiki and Schmitt (1986) linked this pattern to general water-quality parameters, such as total alkalinity and specific conductance, that indicate irrigation return flows. The results of this study parallel Saiki and Schmitt's (1986) results for biota; however, the uppermost San Joaquin River sites sampled by Saiki and Schmitt (1986) were not sampled in this study. The reference and east-side sites are probably most similar to their upper sites (fig. 1). A similar pattern of low concentrations of organochlorine compounds at the reference and east-side sites and higher concentrations at the downstream sites was found in this study. Concentrations of ΣDDT in biota

Table 6. Trends in concentration of ΣDDT in tissue (µg/kg wet weight) over time at the same or nearby sites, San Joaquin River drainage, California

[Comparisons are for *Corbicula* tissue (Rasmussen and Blethrow, 1990), except for the San Joaquin near Patterson where concentrations in carp tissue are compared (Saiki and Schmitt, 1986). Data from this study are listed under 1992. --, no data]

Site	Year					
	1978	1979	1980	1981	1985	1992
Kings River at Peoples Weir	106.0	184.0	193.0	--	--	16.0
Merced River near Stevinson ¹	69.0	--	49.0	--	52.0	22.0
Tuolumne River at Modesto.....	--	--	--	--	10.0	14.0
Stanislaus River near Ripon ²	131.0	--	40.0	--	--	6.1
Mokelumne River near Woodbridge.....	96.0	--	17.0	--	--	5.8
San Joaquin River near Patterson ³	--	--	--	1,288.0	--	509.9
San Joaquin River near Vernalis	--	--	--	--	1,225.0	295.4

¹Comparison data were actually from the Merced River at George Hatfield State Park in 1985, about 5.6 km downstream of the site sampled in 1992, and the Merced River at Hagaman County Park, about 8.8 km upstream of the site sampled in 1992

²Comparison data were actually from the Stanislaus River at Caswell State Park, about 12.3 km downstream of the site sampled in 1992

³Values for ΣDDT are the sum of *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD at both sites for this comparison only

and TOC-normalized sediment were correlated with water-quality parameters that indicate the contribution of agricultural return flows to stream discharge.

The comparability of tissue concentrations in *Corbicula* and fish tissue has not been rigorously established, but past data in Rasmussen and Blethrow (1990) suggest that such comparisons are not unreasonable. At sites where *Corbicula* and fish fillets were simultaneously collected from the same site, the ratios of Σ DDT in *Corbicula* to Σ DDT in fish tissues were as follows: white catfish (*Ameiurus catus*) fillets, 0.24 to 1.00 (mean=0.63, n=4); channel catfish (*Ictalurus punctatus*) fillets, 0.06 to 0.84 (mean=0.35, n=4); largemouth bass (*Micropterus salmoides*) fillets, 1.38 to 8.76 (mean=4.69, n=5); and carp fillets, 0.15 to 2.19 (mean=1.36, n=5). The wide range of these data suggests that comparisons of *Corbicula* data with national data gathered from fish fillets from a variety of fish species would be as valid as comparisons made with a single species of fish. However, comparisons of *Corbicula* data with whole fish values may be conservative because concentrations in whole fish exceed those in fillets.

Though lower than concentrations measured in the 1970s and 1980s, concentrations of *p,p'*-DDE in biota from west-side tributary sites, San Joaquin River sites (SJ2, SJ3), Salt Slough, and Mud Slough (fig. 1) were high compared to concentrations found during

two national studies of contaminants in tissues (fig. 7). The National Study of Chemical Residues in Fish (NSCRF) collected composite samples of whole bottom fish and predatory game fish fillets during 1987 (U.S. Environmental Protection Agency, 1992). The National Contaminant Biomonitoring Program (NCBP) of the U.S. Fish and Wildlife Service collected composite samples of whole bottom fish and whole predatory fish during four time periods (1976-1977, 1978-1979, 1980-1981, and 1984) (Schmitt and others, 1990). Geometric mean concentrations of *p,p'*-DDE during these time periods were 260, 240, 200, and 190 $\mu\text{g}/\text{kg}$, respectively. *Corbicula* from site at the San Joaquin River near Vernalis (SJ3) (fig. 1) exceeded only the latter two values.

Similarly, all west-side sites exceeded geometric mean concentrations of *p,p'*-DDT found during the NCBP study (range of 30 to 50 $\mu\text{g}/\text{kg}$ over the different time periods) (table 5). The San Joaquin River near Vernalis site (SJ3) exceeded only the 1984 geometric mean (30 $\mu\text{g}/\text{kg}$) (table 5). Only the Orestimba Creek site (WS1) (fig. 1) exceeded the geometric mean concentrations for *p,p'*-DDD (range of 60 to 80 $\mu\text{g}/\text{kg}$ over different time periods). Concentrations of Dachthal' (DCPA) at the west-side tributary sites and the two most downstream

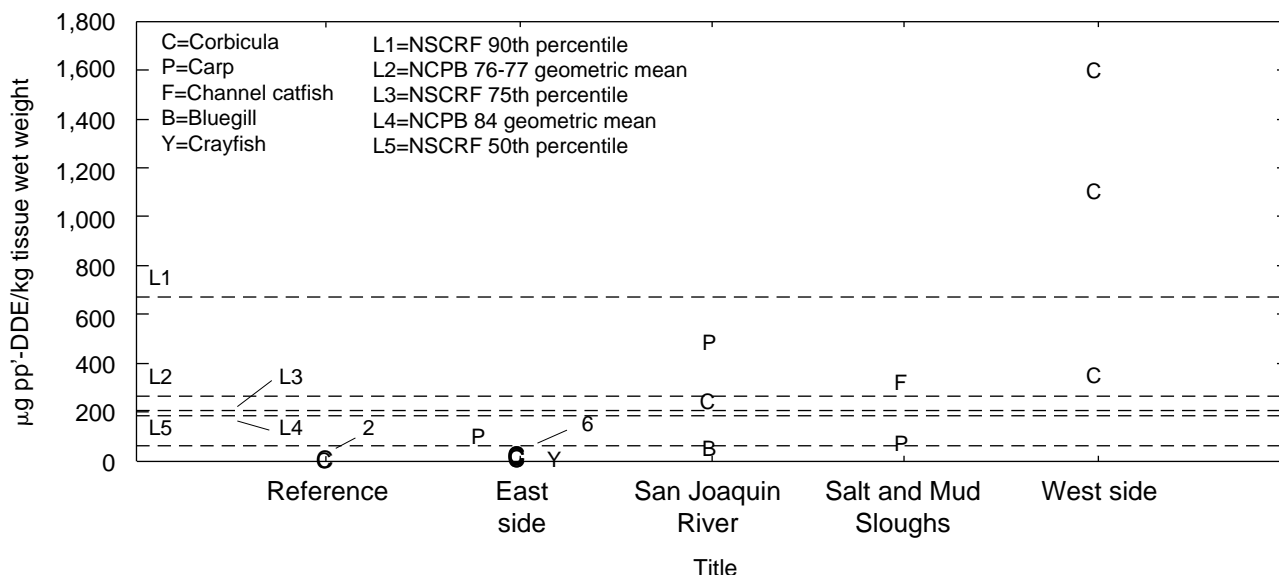


Figure 7. Concentrations of *p,p'*-DDE in tissue (wet weight) compared to the 50th, 75th, and 90th percentiles from the National Study of Chemical Residues in Fish (NSCRF) conducted by the EPA (1992, composite samples of whole bottom fish and fillets of predatory gamefish collected in 1987) and to geometric mean concentrations from the National Contaminant Biomonitoring Program of the U.S. Fish and Wildlife Service in 1976-1977 and 1984 (Schmitt and others, 1990, composite samples of whole bottom fish and whole predatory fish).

San Joaquin River sites exceeded all NCBP geometric mean concentrations (maximum of 10 µg/kg). Concentrations of toxaphene at Orestimba Creek (WS1) and Spanish Grant Drain (WS2) exceeded all NCBP geometric mean values (range of 140 to 340 µg/kg over different time periods), but the San Joaquin River near Vernalis site (SJ3) only exceeded the 1984 value (140 µg/kg). The chemical concentrations found in this study may be even higher, relative to present day concentrations in the Nation, because concentrations of organochlorine compounds in tissues have probably declined nationally since 1984. For example, over the life of the NCBP, declines in geometric mean concentrations from 1976-1984 were noted for all *p,p'*-homologs of DDT and toxaphene (Schmitt and others, 1990).

The only previous comprehensive study of bed sediments (Gilliom and Clifton, 1990) documented a pattern of distribution similar to this study and indicated that the most contaminated sediments occurred in the west-side tributaries. Contaminant concentrations in the east-side tributaries were generally low, and the San Joaquin River near Vernalis was intermediate. The maximum concentrations Gilliom and Clifton (1990) observed for DDT compounds generally were higher than observed during this study, but maximum concentrations of other compounds were lower than observed in this study. However, several of Gilliom and Clifton's (1990) highest values came from streams not sampled in this study.

When concentrations of ΣDDT found in this study were compared to values found by Gilliom and Clifton (1990) at the same or nearby sites, the values in this study were consistently lower as would be expected if bed sediment concentrations were declining over time (table 7); however, differences in sample collection technique may be partially responsible for the absence of decline of other compounds. Gilliom and Clifton (1990) composited samples from several points along a transect across the stream rather than concentrating on recently deposited, near-shore, fine sediment. If their composites mixed recently deposited, near-shore, fine sediments that had high concentrations of compounds with other sediments that had lower concentrations, their results would be biased downward compared to this study.

Gilliom and Clifton (1990) compared their results from the San Joaquin River near Vernalis (SJ3) (fig. 1) with those of a study of sediment contamination conducted by the USGS from 1975 to 1979 at 172 National Pesticide Monitoring Network (NPMN) sites on rivers in the United States (Gilliom and others, 1985) and concluded that the San Joaquin River had some of the highest concentrations of organochlorine residues in bed sediments among the major rivers of the United States. Concentrations at the San Joaquin River near Vernalis (SJ3) in 1992 were still high, compared to median concentrations at NPMN stations, whether the medians are calculated using all sites or only sites with detections. In 1992, the concentration of DDD was 2.9 µg/kg dry weight (compared to

Table 7. Comparisons of concentrations of ΣDDT in sediment between Gilliom and Clifton (1990) in 1985 and this study in 1992 at the same or nearby sites

[Comparisons are made on the basis of dry weight concentration (DW, µg/kg sediment) and concentration normalized to total organic carbon (CW, µg/kg total organic carbon)]

Site	1985		1992	
	DW	CW	DW	CW
Merced River near Stevinson (ES3).....	57.1	10,196.0	1.6	145.5
Tuolumne River at Modesto (ES4)	0.1	125.0	49.5	5,380.4
Stanislaus River near Ripon (ES7).....	4.8	872.7	1.5	157.9
Orestimba Creek at River Road (WS1) ¹	665.0	120,909.1	415.0	56,081.1
Del Puerto Creek at Vineyard Road (WS3) ²	102.0	9,272.7	120.1	14,129.4
Salt Slough at Lander Avenue (MS1)	19.2	1,371.4	4.5	681.8
Mud Slough near Gustine (MS2)	2.0	869.6	1.4	194.4
San Joaquin River near Stevinson (SJ1)	1.5	217.4	0	0
San Joaquin River near Vernalis (SJ3).....	11.6	3,411.8	13.2	2,538.5

¹Comparison data were actually from Orestimba Creek near Highway 33 about 7.1 km upstream of the site sampled in 1992

²Comparison data were actually from Del Puerto Creek near Highway 33 about 1.5 km upstream of the site sampled in 1992

NPMN medians of 0.5 and 2.2 $\mu\text{g}/\text{kg}$, respectively), DDE was 7.9 $\mu\text{g}/\text{kg}$ dry weight (compared to 0.3 and 1.5 $\mu\text{g}/\text{kg}$, respectively), and DDT was 2.4 $\mu\text{g}/\text{kg}$ dry weight (compared to 0.5 and 2.4 $\mu\text{g}/\text{kg}$, respectively). Concentrations of compounds found in 1992 were similar to Gilliom and Clifton's (1990) results from this site for DDD (3.2 $\mu\text{g}/\text{kg}$), DDE (7.1 $\mu\text{g}/\text{kg}$), and DDT (1.3 $\mu\text{g}/\text{kg}$). Gilliom and Clifton (1990) found chlordane and dieldrin at this location, but these compounds were not detected at this site in this study. Conversely, toxaphene was detected at this site in this study but not in Gilliom and Clifton's (1990) study. Overall, it appears that concentrations of organochlorine compounds, particularly DDT compounds, have remained high relative to national values in both tissues and sediments.

The differences in concentrations of ΣDDT among regions did not parallel differences in lipid content of tissues or TOC in sediment. The size of clams and carp differed among sites, but size differences did not follow any regional order, except for San Joaquin River *Corbicula*, which were especially large. It seems unlikely that the differences among reference sites, west-side tributaries, and east-side tributaries can be attributed simply to the size of organisms. The TOC content of sediment also varied among regions, but the highest values were found at the reference sites where no compounds were detected and at the east-side tributaries where concentrations were low (table 4). Presumably, the reservoirs upstream of the reference and east-side sites were acting as sediment traps, and most fine sediment consisted of organic materials, such as decomposing algae, with high TOC content.

The use of most organochlorine pesticides in the United States had already been greatly reduced or eliminated prior to the early 1970s (Gilliom and others, 1985) when pesticide-use records were first kept in California (Mischke and others, 1985). It is difficult to link the environmental concentrations found in this study to patterns of past use. However, the use of these compounds, particularly DDT, was widespread in intensively farmed areas like the San Joaquin Valley (Mischke and others, 1985).

The differences in concentrations of ΣDDT in sediment among regions can be most likely attributed to differences in past use of DDT or differences in hydrology. Levels at reference sites are low because

they are located above agricultural areas where pesticide use is high. East-side soils are porous, and most irrigation water percolates into the soil before entering the rivers, minimizing transport of soils with high concentrations of environmentally persistent pesticides to surface water. River discharge also tends to be higher in the east-side tributaries so irrigation return flows tend to be diluted, resulting in better overall water quality. The west side of the valley has been farmed since the early 1900s and was intensely farmed during the period when DDT was commonly used (Gilliom and Clifton, 1990). Historically, these streams were intermittent or ephemeral with little or no flow entering the San Joaquin Valley from the Coast Ranges. Therefore, most of the water in west-side tributaries consists of irrigation return water, and most of the sediment is derived from farmed soils that would likely carry high concentrations of environmentally persistent pesticides. Mud and Salt Sloughs also are located on the west side of the San Joaquin Valley, but the large areas of managed wetlands in the area probably resulted in lower use of pesticides in these drainages. Part of the water that reaches these streams also is derived from subsurface (tile) drains. This water has been filtered through soil at low velocities and generally does not contain high levels of particulate matter (Gilliom and Clifton, 1990). The two most downstream San Joaquin River sites were intermediate between the different tributaries because they integrated inputs from both sides of the valley.

Concentrations of ΣDDT in biota appear to be determined by the processes described above for transport of contaminated soils into streams. The significant regression between ΣDDT content of sediment and tissue suggests a relation between the two media; however, use of silt-normalized data tended to decrease the strength of the relation, and use of TOC-normalized data tended to increase the strength of the relation. A likely hypothesis is that silt content is a better indicator of overall concentration of ΣDDT , and TOC content is a better indicator of bioavailability of ΣDDT . The first assumption is supported by the significant correlation of silt with ΣDDT . The second assumption is supported by the greater proportion of the variance explained for the total data set when TOC-normalized data were used in the regression. *Corbicula* are filter feeders and consume fine particulate organic matter that may be rich in adsorbed chemicals, depending on the source area. Carp and

catfish are bottom feeders and consume sediment-associated invertebrates that feed on particulate organic matter. Bluegill and crayfish are less directly associated with bed sediment, but this study only included one sample of each. Though suspended organic matter and inorganic sediment were not analyzed directly in this study, recently deposited bed sediment can represent recently settled suspended material and bed material available for resuspension and consumption by organisms. Pereira and others (1996) documented a nearly 1:1 relation between TOC-normalized concentrations of eight organochlorine compounds in bed sediment and suspended sediment in samples collected from Orestimba Creek (WS1) at the same time as samples collected for this study.

A close relation between concentrations of chemicals in bed sediment and tissue is unusual, though most studies testing such relations tend to focus on trace elements (Elder and Matraw, 1984; Johns and others, 1988; Luoma and others, 1990). Rowan and Rasmussen (1992) found relations between tissue concentrations of organochlorine chemicals in fish and concentrations in other media, including bed sediment, but the relation was dependent on a number of environmental factors. Some studies have linked the health of biota with contamination of sediment (Baumann and others, 1991; Manny and Kenaga, 1991; Stein and others, 1992). Pereira and others (1988) found that the relations between the concentrations of halogenated organic compounds in water and suspended sediment with concentrations in lipid of biota were stronger than the relation between concentrations in bed sediment and biota. The relation between concentrations in bed sediment and biota in the present study was likely due to the wide range in Σ DDT concentrations found among regions. For example, exclusion of the west-side sites would have made the finding of a significant regression much more dependent on variation among sites within the east-side tributary group. The effect of the high concentration of Σ DDT in sediment at the Tuolumne River in Modesto (ES4) (fig. 1) on the regression also would have been much greater.

The most anomalous data in the relation between tissue and sediment were from the Tuolumne River in Modesto (ES4) (table 5; the point in the lower right quadrant of fig. 6). The concentration of Σ DDT in sediment was very high in comparison to the

concentration found in the sample of *Corbicula* and to the sediment concentrations from other east-side sites. Gilliom and Clifton (1990) also collected a sample from an east-side tributary (Merced River near Stevinson, ES3) (fig. 1) with high concentrations of DDT compounds relative to the other east-side sites. In the present study, more compounds were detected in sediment from the Tuolumne River site than any other east-side site (table 5). These data suggest that contaminated soils occasionally enter the east-side tributaries, but the location of the bed sediments is highly variable in time and space. The substrate of all of the east-side tributaries is dominated by sand in the areas sampled (table 4), and the fine bed sediments collected were restricted to small patches. In addition, discharge in the east-side tributaries is highly regulated, and short-term increases in discharge for water management purposes may have substantial effects on scouring and deposition of these small depositional areas.

SUMMARY

The results of this study do not indicate any clear advantage to using biota or sediment in contaminated studies. Sediment is available in most streams, but most regulatory agencies are interested in bioaccumulation of compounds in biota and the associated health risks to humans and wildlife that consume contaminated biota. Toxaphene, DDT compounds, and PCBs were detected more consistently in biota, but other compounds never or rarely detected in tissue were more frequently detected in sediment. No compounds were detected at reference sites, linking detectable concentrations to human activities. Concentrations of organochlorine compounds in the biota, and perhaps in the bed sediments, of the San Joaquin Valley streams appear to have declined from levels measured in the 1970s and 1980s, but concentrations in both media remain high in some areas compared to other regions of the United States. Both media had different concentrations of Σ DDT among streams throughout the San Joaquin Valley, and those differences were consistent with earlier studies. Concentrations were particularly high in the west-side tributaries to the San Joaquin River. Regression analysis suggested a good link between sediment and TOC-normalized sediment concentrations and concentrations in tissue. A likely hypothesis is that

concentrations of Σ DDT in sediment are controlled by transport of contaminated soils into streams and that TOC content of the resulting sediment affects uptake by biota. Concentrations of some organochlorine chemicals in tissue and sediment did exceed guidelines established for the protection of the aquatic environment. Recent studies suggest that hormonal disruption caused by these chemicals presents a previously unknown hazard to both humans and wildlife (Fox, 1992; Leatherland, 1992; Reijnders and Brasseur, 1992; Thomas and Colborn, 1992) and may refocus attention on these chemicals in the near future.

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