Excessive Bioaccumulation of Organochlorine Legacy Pesticides & PCBs in CA Central Valley Fish

G. Fred Lee, PhD, PE, DEE & Anne Jones-Lee, PhD
G. Fred Lee & Associates
El Macero, CA
gfredlee@aol.com www.gfredlee.com

Organochlorine Pesticides & PCBs "OCls"

Nature of Excessive OCl Bioaccumulation Problem

US EPA Water Quality Criteria

OEHHA Fish Tissue Guidelines

TMDLs to Control Excessive Bioaccumulation

Made Available at US EPA National Fish Contaminant Forum, San Diego, CA January (2004)

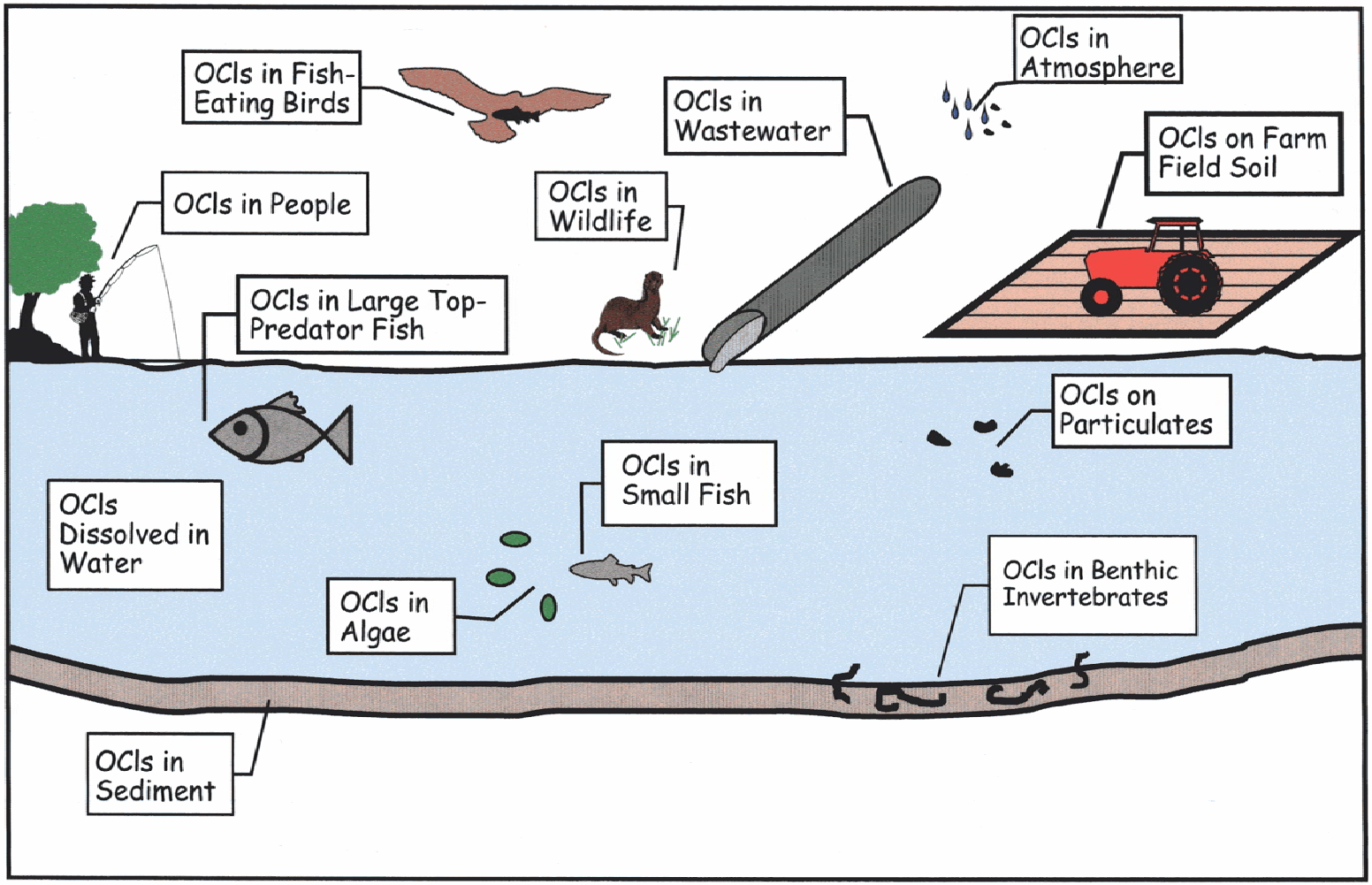
Overview

- Introduction
  - Organochlorine Pesticides & PCBs “OCls”
  - Nature of Excessive OCl Bioaccumulation Problem
    - US EPA Water Quality Criteria
    - OEHHA Fish Tissue Guidelines
  - TMDLs to Control Excessive Bioaccumulation
- Sources of OCls
  - Current Ag Runoff vs Waterbody Sediments

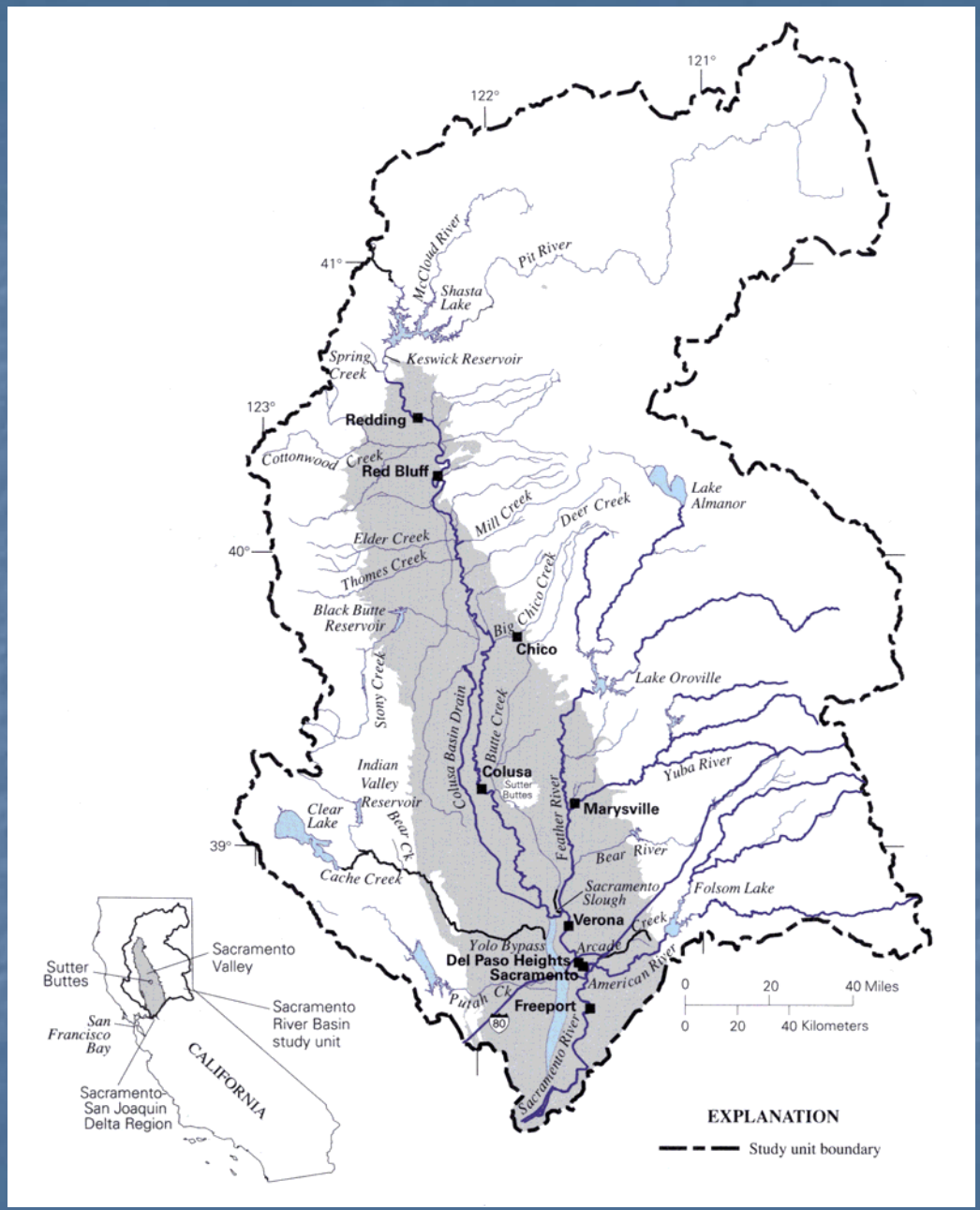
Overview

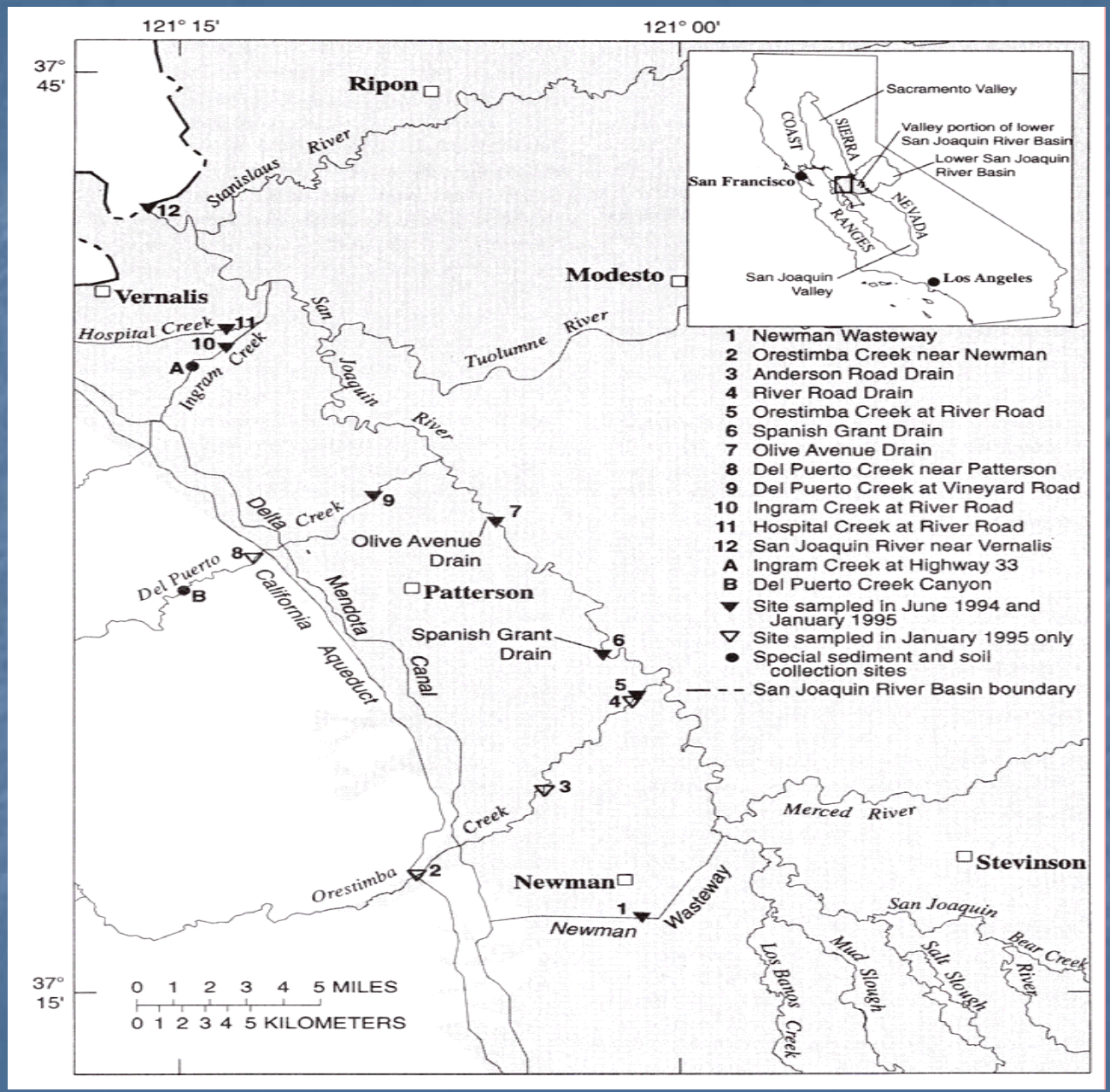
- Bioavailability of OCls
  - Not All OCls in Sediments Are Bioavailable – TOC Binding
  - Smith Canal PCB Studies
    - US EPA Benthic Organism Uptake Studies
- Control Programs
  - For Current Ag Input -- Control Erosion from Ag Lands
    - PAM Use of Westside of San Joaquin River
  - Dredging of Toxic Hot Spots of OCls That Are Significant Source
  - Addition of Activated Carbon to Bind OCls in Sediments
  - Need for Funding to Demonstrate That Excessive Bioaccumulation of OCls Can Be Controlled

Conceptual Model of OCl Bioaccumulation



Map Sacramento River Watershed





Map of San Joaquin River Watershed

Conceptual Model of OCl Excessive Bioaccumulation Components

- Central Valley Waterbody Watersheds
  - OCls in Former Agricultural & Urban OCl Use Areas
  - Runoff/Discharges in Stormwater Runoff & Tailwater Discharges
    - Primarily Associated with Transport of Particulates
  - Atmospheric Loads
- Central Valley Waterbodies
  - OCl Uptake by Aquatic Life (Animals & Plants) from Sediments & Water -- Food Web Bioaccumulation
    - Benthic Macro-Invertebrates $\rightarrow$ Small Animals & Fish $\rightarrow$ Larger Fish $\rightarrow$ Top Game Fish; Predators with High Lipids
- Impacts
  - Use of Fish as Food by Humans, Terrestrial Animals & Birds
- OCl Bioaccumulation Database - 4x6-ft Excel Spreadsheet

Excessive Bioaccumulation of OCl in CA Central Valley Fish

- 1998 -- 11 Waterbodies in CV Deemed “Impaired” by Clean Water Act 303(d) Due to Excessive Bioaccumulation of OCl “Group A” Pesticides Such as
  - Toxaphene, Chlordane, Dieldrin, Aldrin, Endrin, Heptachlor, Heptachlor Epoxide, Hexachlorocyclohexane [Including Lindane], Endosulfan
  - DDT, DDE, DDD, PCBs, Dioxins
- Waterbodies Impacted Include
  - Delta Waterways Lower American River, Colusa Basin Drain, Lower Feather River, Lower Merced River, Natomas East Main Drain, San Joaquin River, Lower Stanislaus River, Stockton Deep Water Ship Channel, Lower Tuolumne River, Lower Kings River
- Other Waterbodies in Central Valley (e.g., Sacramento River) Not Now on 303(d) “Impaired” List But That Contain Fish with Excessive Levels of Organochlorine Pesticides & PCBs
  - Based on Information Available; Could Be Added to List

Fresh Water Watercolumn Target Values for Organochlorine Compounds

Constituent	Freshwater		Human Health (10^{-6} risk for carcinogens) For consumption of:	
	CMC (acute) (µg/L)	CCC (chronic) (µg/L)	Water & Organisms (µg/L)	Organisms Only (µg/L)
Aldrin	3	--	0.00013	0.00014
Chlordane	2.4	0.0043	0.00057	0.00059
DDT*	1.1	0.001	0.00059	0.00059
Dieldrin	0.24	0.056	0.00014	0.00014
Endosulfan	0.22	0.056	110	240
Endrin	0.086	0.036	0.76	0.81
Heptachlor	0.52	0.0038	0.00021	0.00021
Heptachlor Epoxide	0.52	0.0038	0.00010	0.00011
Hexachlorocyclohexane (including lindane), gamma-BHC	0.95	--	0.019	0.063
PCBs	--	0.014	0.00017	0.00017
Toxaphene	0.73	0.0002	0.00073	0.00075
Dioxins/Furans	--	--	0.000000013	0.000000014

Source: US EPA (2000b)

-- no value provided

Criteria are based on carcinogenicity of 10^{-6} risk.

* DDT value cited for 4,4' DDT, but value will apply to one isomer or sum of all isomers detected.

Potential Fish Tissue OCl Goals for Human Health Protection

An acceptable level of OCl in fish tissues can be calculated using equation

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

Units in this equation are:

$$\mu\text{g OCl/g fish (mg/kg)} = \frac{\mu\text{g OCl/kg bwt/day} * \text{kg bwt}}{\text{g fish/day}}$$

Where:

OCl = organochlorine pesticide, DDT, PCB, or dioxin/furan
g = gram,
µg = microgram,
kg = kilogram
bwt = consumer's body weight

The acceptable daily intake is the quantity at or below which humans consuming the fish containing the OCl are expected to be protected from adverse effects.

US EPA & OEHHA Fish Tissue Screening Values

CHEMICAL	US EPA Value[1] (µg/kg wet weight)	OEHHA Value[2] (µg/kg wet weight)
Chlordane[3]	80	30
Total DDT[4]	300	100
Dieldrin	7	2
Total endosulfan[5]	60,000	20,000
Endrin	3000	1000
Heptachlor epoxide	10	4
γ-hexachlorocyclohexane (lindane)	80	30
Toxaphene	100	30
PCBs[6]	10	20
Dioxin TEQ[7]	0.7 ppt	0.3 ppt

Source: SARWQCB (2000)

1: USEPA SVs (US EPA, 1995a) for carcinogens were calculated for a 70 kg adult using a cancer risk of 1x10-5. SVs for non-cancer effects were calculated for a 70 kg adult and exposure at the RfD (hazard quotient of 1). A fish consumption value of 6.5 g/day was used in both cases.

2: California OEHHA (1999) SVs (CLS-SVs) specifically for this study were calculated according to US EPA guidance (US EPA, 1995a). CLS-SVs for carcinogens were calculated for a 70 kg adult using a cancer risk of 1x10-5. CLS-SVs for non-cancer effects were calculated for a 70 kg adult and exposure at the RfD (hazard quotient of 1). A fish consumption value of 21 g/day was used in both cases

3: Sum of alpha and gamma chlordane, cis- and trans-nonachlor and oxychlordane.

4: Sum of othro and para DDTs, DDDs and DDEs.

5: Sum of endosulfan I and II.

6: Expressed as the sum of Aroclor 1248, 1254 and 1260.

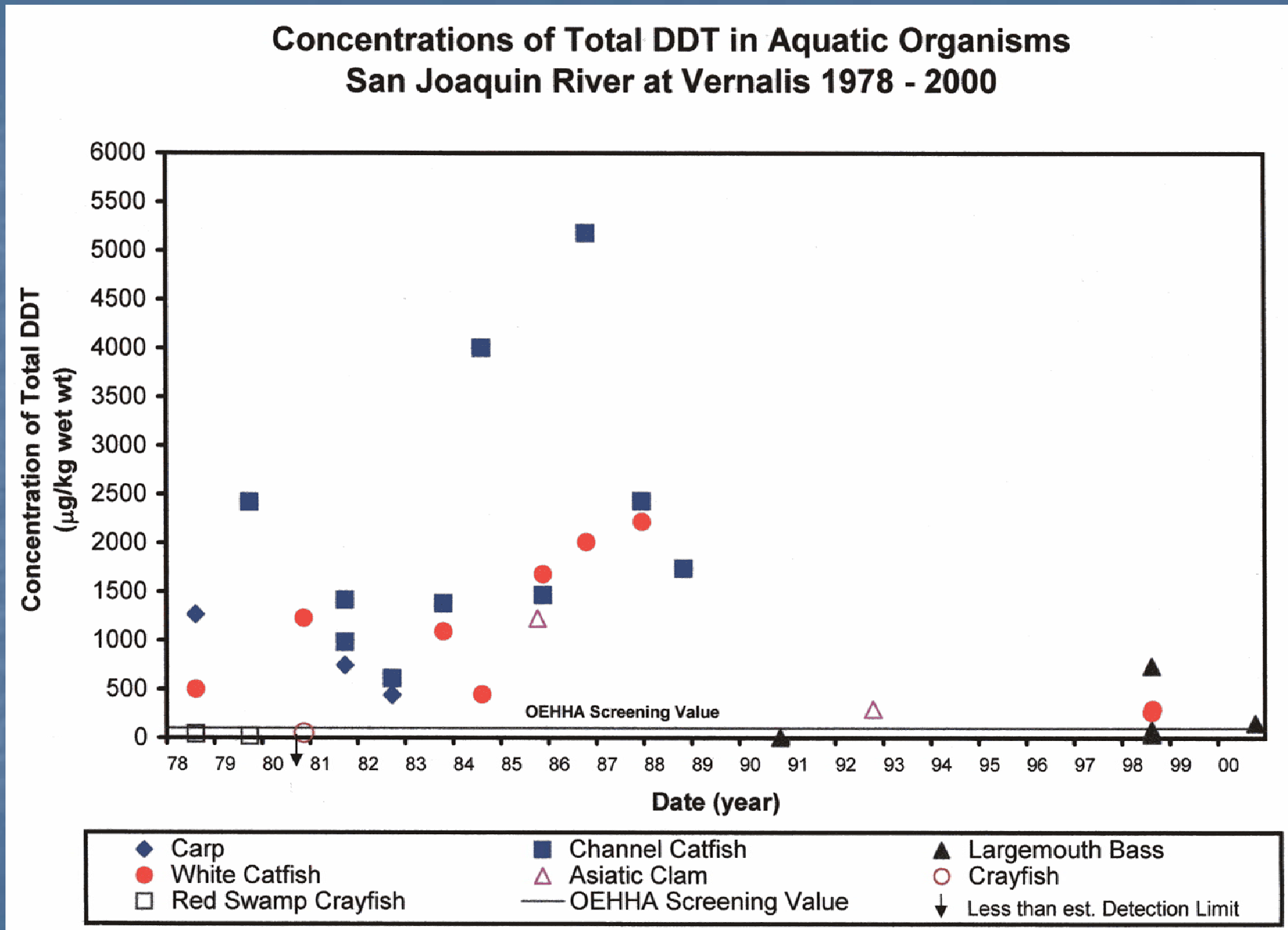
7: Expressed as the sum of TEQs for dibenzodioxin and dibenzofuran compounds which have an adopted TEF.

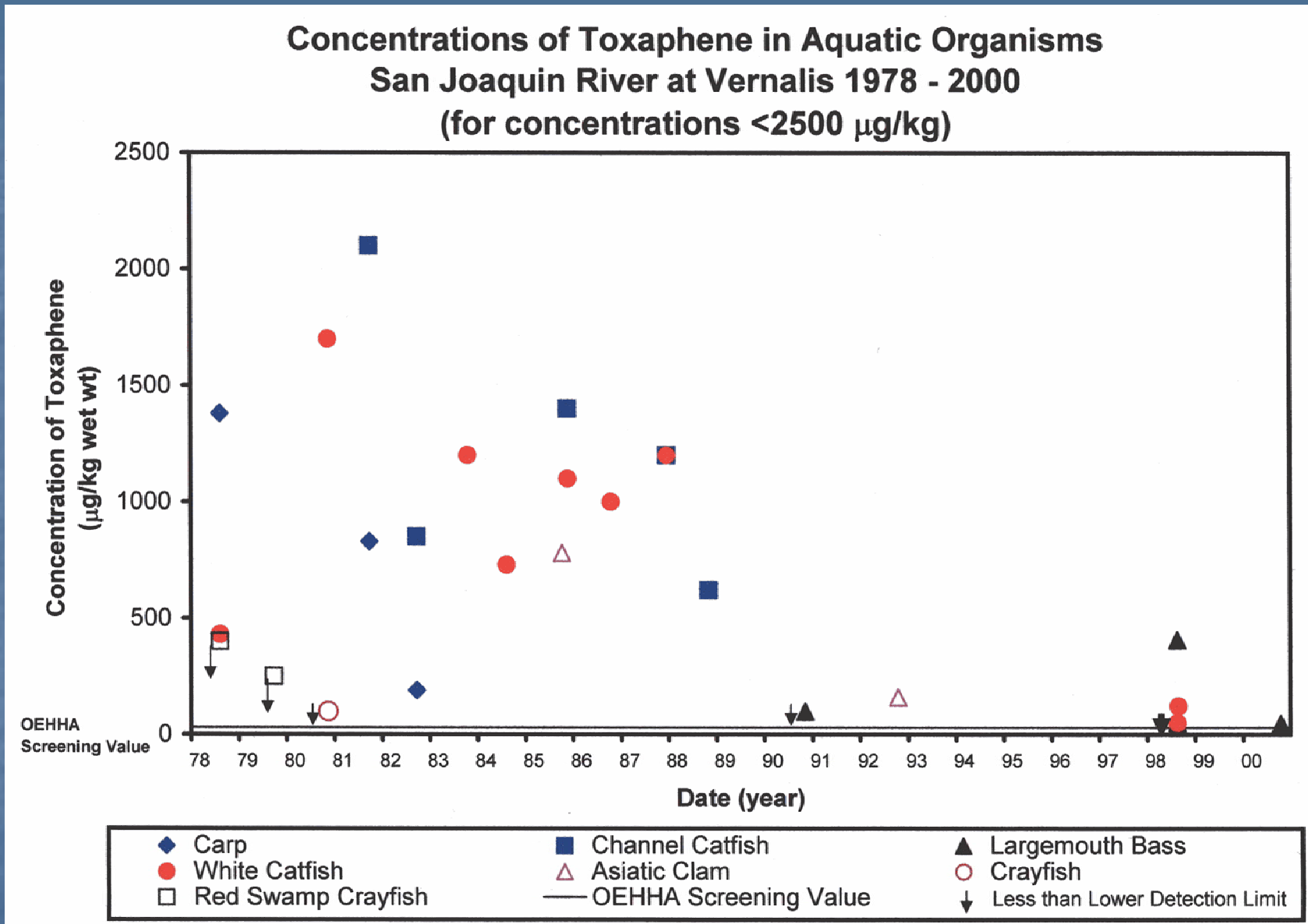
Biota/Sediment Accumulation Factors (BSAFs)

- In US EPA (1995a) BSAFs Defined as
  - Ratio of
    - Substance's Lipid-Normalized Concentration in Tissue of Aquatic Organism to Its Organic Carbon-Normalized Concentration in Surface Sediment
  - In Situations Where
    - Ratio Does Not Change Substantially Over Time
    - Both Organism & Food Exposed
    - Surface Sediment Is Representative of Average Surface Sediment in Vicinity of Organism
- Site-Specific BSAFs (kg Organic C/kg Lipid) Calculated for NonPolar Organic Compounds Using Formula:

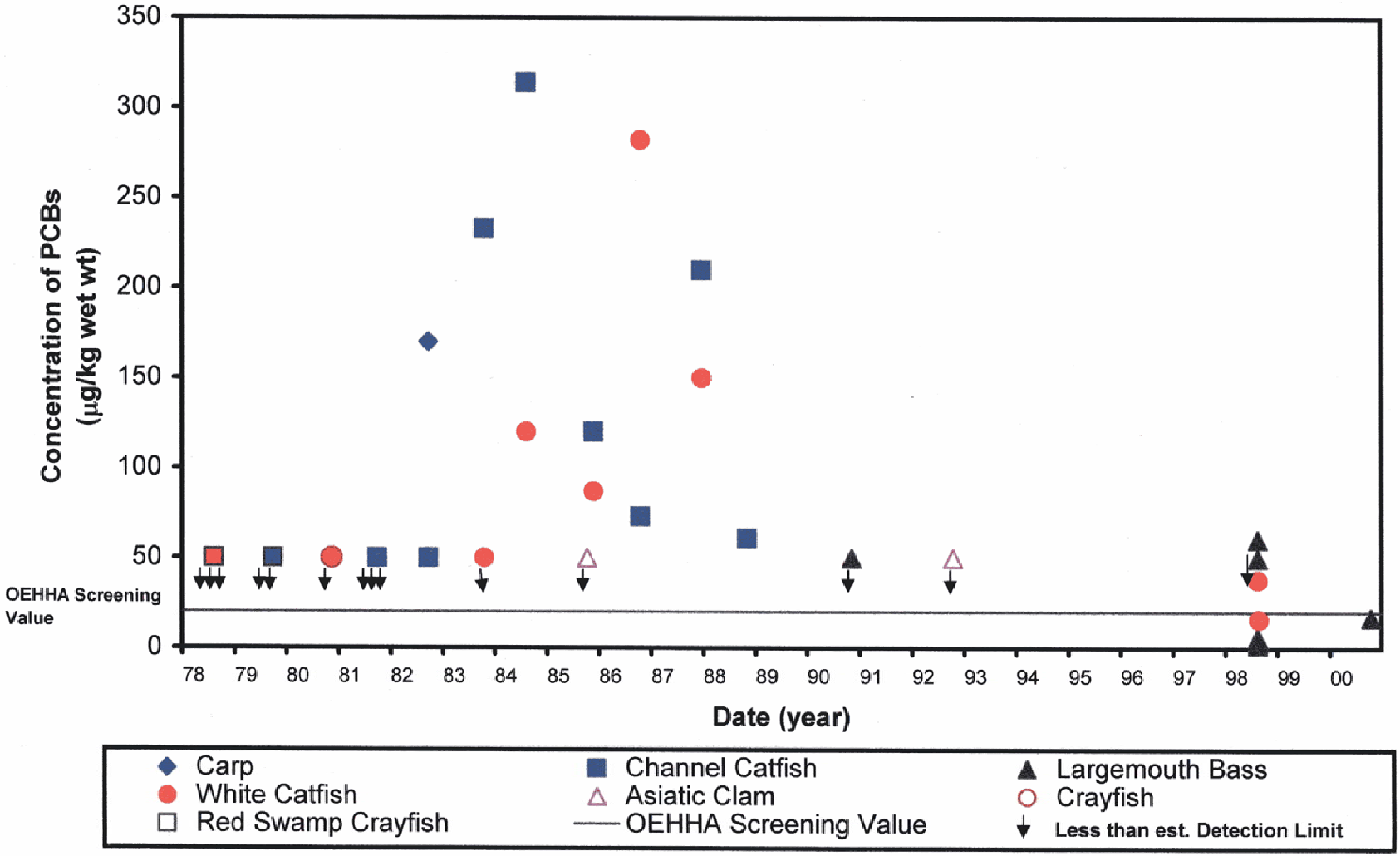
$$BSAF = (Ct/f1) / (Cs/foc)$$

Ct = Contaminant Concentration in Organism
f1 = Lipid Fraction in Tissue
Cs = Contaminant Concentration in Sediment
foc = Organic Carbon Fraction in Sediment

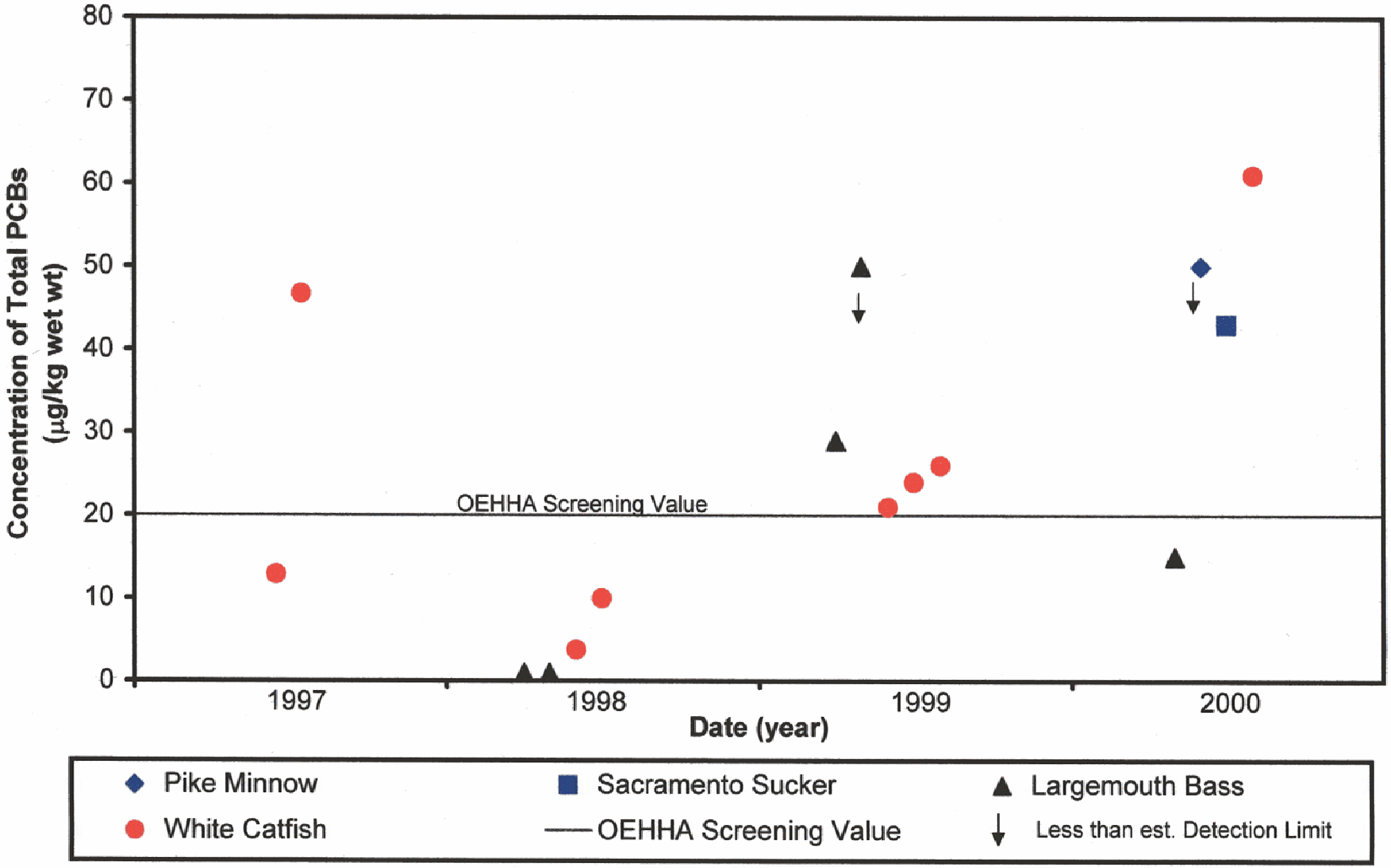

Concentrations of Total DDT in Aquatic Organisms
San Joaquin River at Vernalis 1978 - 2000
Concentration of Total DDT (µg/kg wet wt)
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
OEHHA Screening Value
78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00
Date (year)
Carp
White Catfish
Red Swamp Crayfish
Channel Catfish
Asiatic Clam
OEHHA Screening Value
Largemouth Bass
Crayfish
Less than est. Detection Limit

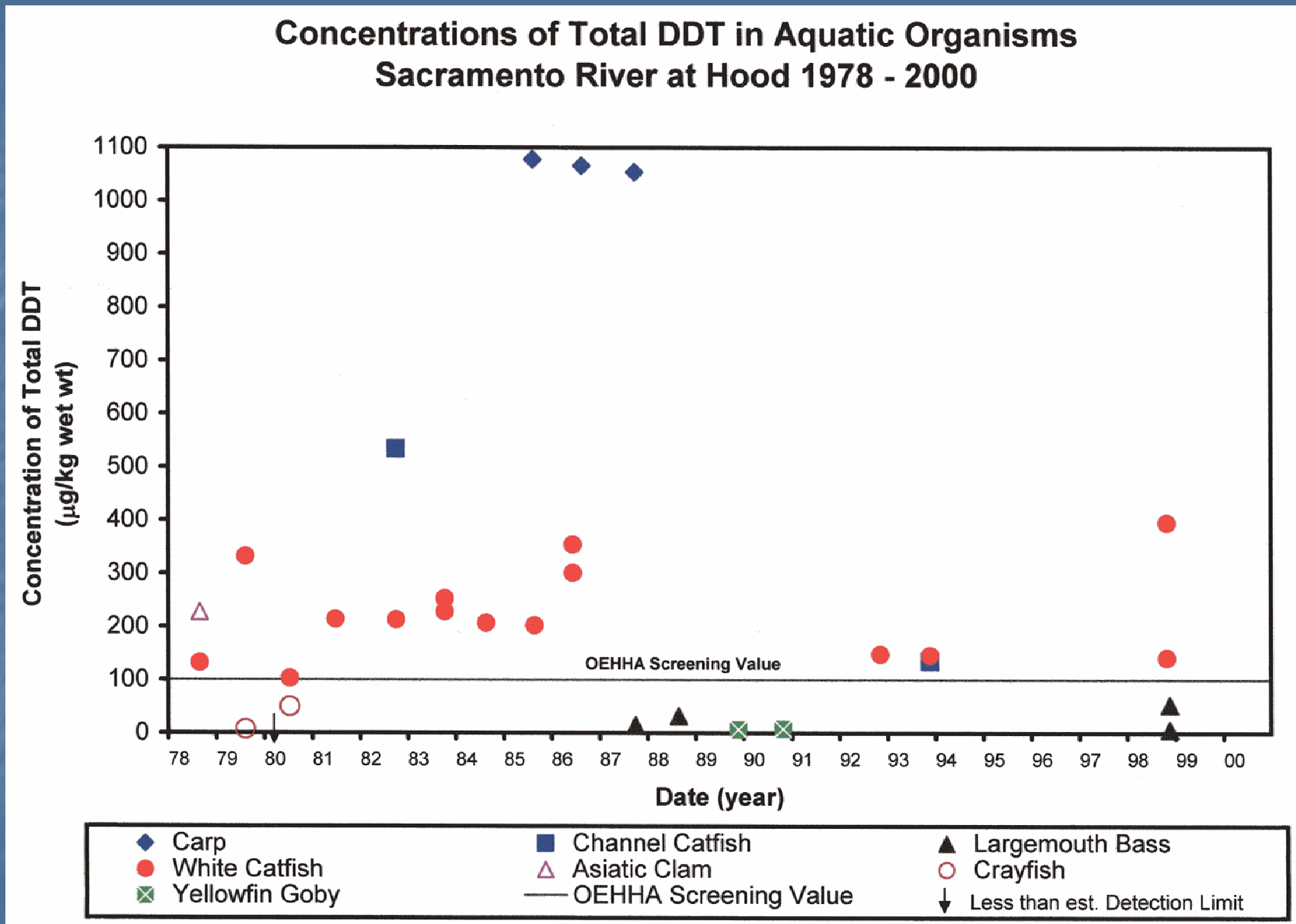

Concentrations of Toxaphene in Aquatic Organisms
San Joaquin River at Vernalis 1978 - 2000
(for concentrations <2500 µg/kg)
Concentration of Toxaphene (µg/kg wet wt)
2500
2000
1500
1000
500
0
OEHHA Screening Value
78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00
Date (year)
Carp
White Catfish
Red Swamp Crayfish
Channel Catfish
Asiatic Clam
OEHHA Screening Value
Largemouth Bass
Crayfish
Less than Lower Detection Limit

Concentrations of Total PCBs in Aquatic Organisms
San Joaquin River at Vernalis 1978 - 2000



Concentrations of Total PCBs in Aquatic Organisms
Sacramento River at Mile 44 1997 - 2000




Concentrations of Total DDT in Aquatic Organisms
Sacramento River at Hood 1978 - 2000
Concentration of Total DDT (µg/kg wet wt)
1100
1000
900
800
700
600
500
400
300
200
100
0
OEHHA Screening Value
78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00
Date (year)
Carp
White Catfish
Yellowfin Goby
Channel Catfish
Asiatic Clam
OEHHA Screening Value
Largemouth Bass
Crayfish
Less than est. Detection Limit

Concentrations of p,p'-DDE & Dieldrin in Selected SJR Westside Tributaries during Irrigation Season (June 22, 1994)

Concentrations of p,p'-DDE and Dieldrin in Selected SJR Westside Tributaries During Irrigation Season (June 22, 1994)

Site	Flow (cfs)	Suspended Sediment Concentration (mg/L)	On Suspended Sediment (µg/kg)		Dissolved in Water Column (µg/L)		Concentration in Water Column (µg/L)	
			P,p'-DDE	dieldrin	p,p'-DDE	dieldrin	p,p'-DDE	dieldrin
Newman Wasteway	10	50	61	<4.0	<0.006	<0.001	0.003	<0.0002
Orestimba Creek at River Rd	9.6	315	290	6.5	0.018	0.012	0.091	0.002
Spanish Grant Drain	27	540	86	4.0	0.006	<0.001	0.046	0.002
Olive Avenue Drain	6 (est)	663	140	2.7	0.009	<0.001	0.093	0.0018
Del Puerto Creek at Vineyard Rd	7.8	90	160	7.6	0.003 (est)	<0.001	0.014	0.0007
Ingram Creek at River Rd	11	1,990	250	7.9	0.012	0.012	0.5	0.016
Hospital Creek at River Rd	32	2,530	310	7.6	0.027	0.013	0.78	0.019
San Joaquin River near Vernalis	1,110	142	150	2.5	<0.006	<0.001	0.021	0.0004

(est) estimated

Adapted from Kratzer (1999)

Concentrations of p,p'-DDE & Dieldrin in Selected SJR Westside Tributaries during Stormwater Runoff Event (January 1995)

Concentrations of p,p'-DDE and Dieldrin in Selected SJR Westside Tributaries During Stormwater Runoff Event (January 1995)

Site	Flow (cfs)	Suspended Sediment Concentration (mg/L)	On Suspended Sediment (µg/kg)		Dissolved in Water Column (µg/L)		Concentration in Water Column (µg/L)	
			p,p'-DDE	dieldrin	p,p'-DDE	dieldrin	p,p'-DDE	dieldrin
Newman Wasteway	14	419	150	<5.0	<0.01	<0.01	0.063	<0.0021
Orestimba Creek at River Rd	51	4,980	269	8.2	0.010	0.005 (est)	1.34	0.041
	26	3,100	290	7.0	0.009 (est)	<0.01	0.899	0.022
	300	--	200	5.5	<0.01	<0.01	--	--
	870	4,760	230	3.6	<0.01	0.006 (est)	1.09	0.017
	1,130	1,920	190	1.4	--	--	0.365	0.0027
	684	1,180	230	1.8	--	--	0.271	0.0021
Spanish Grant Drain	66	4,420	180	6.5	<0.01	<0.01	0.796	0.029
Olive Avenue Drain	31 (est)	2,990	160	2.0	0.009 (est)	<0.01	0.478	0.006
Del Puerto Creek at Vineyard Rd	1,000 (est)	10,500	36	0.5	<0.01	<0.01	0.378	0.005
Ingram Creek at River Rd	257 (est)	4,780	130	2.7	0.006 (est)	<0.01	0.621	0.013
Hospital Creek at River Rd	37 (est)	3,640	200	3.5	0.006 (est)	<0.01	0.728	0.013
San Joaquin River near Vernalis	2,940	511	97	<5.0	<0.01	<0.01	0.05	<0.0026

(est) estimated

Adapted from Kratzer (1999)

Sediment Quality Guidelines

Long & Morgan and MacDonald Co-Occurrence Sediment Guidelines

"NOAA SQUIRT" Values

- Not Reliable for Estimating Sediment Toxicity
- Not Applicable to Bioaccumulation

CA SWRCB so-called "NAS" Values

- Not Valid for Estimating Host Organism Impacts of OCls
- Use US COE ERED and US EPA "Jarvinen, and Ankley" Database on Critical Tissue Concentrations of OCls

Sediment Remediation Approaches

- Natural Remediation
  - Occurs after Use/Discharge Occurs
    - Initially Rapid, but Long-Term Very Slow Decrease
- Dredging of Sediments That Are Significant Sources of Excessive OCI

  Hudson River — Upper Fox River, WI

  New Bedford Harbor — Others
- Adding Activated Carbon to Immobilize
  - Luthy - Stanford University Studies
  - Need Field Evaluation

Land Runoff Sources

- Control Erosion
  - PAM – Effective in Controlling Erosion from SJR West Side Agriculture

Specific Areas Needing Further Study for OCl Bioaccumulation Management Program Development

- **Current Fish Tissue Residues** Determine, for each of the listed Waterbodies, as well as other Central Valley waterbodies, the current degree of edible fish tissue OCl residues. These residues should be compared to OEHHA screening values which have been adjusted for local fish consumption rates. This information is essential to defining the waterbodies within the Central Valley where OCls have bioaccumulated to excessive levels in edible fish.
- **Current Watershed Sources** Determine for each of the listed Waterbodies whether stormwater runoff and/or irrigation tailwater discharges and/or domestic and industrial wastewater discharges are currently contributing sufficient concentrations of the OCl of concern in the Waterbody to be contributing to the excessive bioaccumulation of this OCl(s) in edible fish tissue.
- **Atmospheric Loads** Conduct a quantitative assessment of the current atmospheric loads of the OCls for several of the listed Waterbodies to evaluate the potential significance of this source.
- **Current Sediment Sources** Determine the concentrations of the OCls of concern in the listed Waterbodies and the bioavailability of the sediment-associated OCl residues for food web accumulation that leads to excessive edible tissue residues.
- **Dioxin Problem** Determine the extent of edible fish tissue contamination by dioxins and furans within the Central Valley Waterbodies. Where excessive concentrations are found in edible fish tissue, determine likely sources of the dioxins and furans that are bioaccumulating to excessive levels.
- **Fish Consumption Rate** Since the allowable OCl tissue residue for edible fish is dependent on local waterbody fish consumption rates, it is recommended that, as part of developing the management program for the OCl-listed Waterbodies, representative fish consumption rates for each listed Waterbody be developed.

Specific Areas Needing Further Study for OCl Bioaccumulation Management Program Development

- **Bioavailable OCls in Runoff and Sediments** Special-purpose studies need to be conducted using aquatic organism incubation to determine if domestic wastewaters are a significant source of OCls for certain Central Valley Waterbodies.
- **Use of Clams to Monitor** Studies should be conducted to determine if the bioaccumulation by the freshwater clam *Corbicula fluminea* could be used to evaluate the bioaccumulation that may be occurring in edible fish.
- **Adequate tissue Detection Limits** All fish tissue analyses for the OCls should be conducted with an analytical method detection limit that is at least slightly below the OEHHA human health screening value.
- **Tissue Variability** It is recommended that systematic studies of fish tissue OCl concentrations for the fish types of concern at a particular location be conducted to examine the variability in OCl composition at about the same time and location. This information is essential to understanding whether the apparent changes in OCl composition over time are related to real changes or simply reflect the variability of the data.
- **Relationship to Lipid Content** It is also recommended that all OCl measurements of fish tissue include measurements of the lipid content. This information may be useful to normalize the OCl bioaccumulation based on fish edible tissue lipid content.
- **Funding** Need for Funding to further define problem and to implement control programs

References

- Lee, G. F. and Jones-Lee, A., “Organochlorine Pesticide, PCB and Dioxin/Furan Excessive Bioaccumulation Management Guidance,” California Water Institute Report TP 02-06 to the California Water Resources Control Board/Central Valley Regional Water Quality Control Board, 170 pp, California State University Fresno, Fresno, CA, December (2002). http://www.gfredlee.com/OClTMDLRpt12-11-02.pdf
- Lee, G. F. and Jones-Lee, A., “Developing TMDLs for Organochlorine Pesticides and PCBs,” Environmental Chemistry Division Extended Abstracts, American Chemical Society national meeting, San Diego, California, April (2001).
- Lee, G. F., Jones-Lee, A., and Ogle, R. S., “Preliminary Assessment of the Bioaccumulation of PCBs and Organochlorine Pesticides in *Lumbriculus variegatus* from City of Stockton Smith Canal Sediments, and Toxicity of City of Stockton Smith Canal Sediments to *Hyalella azteca*,” Report to the DeltaKeeper and the Central Valley Regional Water Quality Control Board, G. Fred Lee & Associates, El Macero, CA, July (2002). http://www.gfredlee.com/SmithCanalReport.pdf
- Lee, G. F., “Need for Funding to Support Studies to Control Excessive Bioaccumulation of Organochlorine ‘Legacy’ Pesticides, PCBs and Dioxins in Edible Fish in the Central Valley of California,” Report of G. Fred Lee & Associates, El Macero, CA, July (2003).

References

- Lee, G. F. and Jones-Lee, A., "Unreliability of Sediment Co-Occurrence-Based Approaches for Evaluating Aquatic Sediment Quality," Excerpts from Lee, G. F. and Jones-Lee, A., "Organochlorine Pesticide, PCB and Dioxin/Furan Excessive Bioaccumulation Management Guidance," California Water Institute Report TP 02-06 to the California Water Resources Control Board/Central Valley Regional Water Quality Control Board, 170 pp, California State University Fresno, Fresno, CA, December (2002). http://www.gfredlee.com/UnrelSedCooccur.pdf
- SARWQCB. "Problem Statement for the Total Maximum Daily Load for Toxic Substances in Newport Bay and San Diego Creek, Final." Santa Ana Regional Water Quality Control Board, Riverside, CA, December. (2000)
- US EPA. . "Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume 1, Fish Sampling and Analysis." Second Edition, U.S. Environmental Protection Agency, EPA 823-R-93-002, Washington, D.C. (1995)
- US EPA. . "Bioaccumulation Testing and Interpretation for the Purpose of Sediment Quality Assessment: Status and Needs." U.S. Environmental Protection Agency, EPA-823-R-00-001, Washington, D.C. 2000. http://www.epa.gov/ost/cs/biotesting/
- US EPA. "Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates." Second Edition, U.S. Environmental Protection Agency, EPA/600/R-99/064, Washington, D.C. (2000a)
- US EPA.). "Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Rule." *Federal Register* 40 CFR Part 131, pp. 31682-31719. U.S. Environmental Protection Agency, Washington, D.C. May 18. (2000b)

Further Information

Consult Website of
Drs. G. Fred Lee and Anne Jones-Lee

http://www.gfredlee.com