Monitoring Plan

Tissue Residues of Organochlorine Pesticides and Polychlorinated Biphenyls in Fish Collected from Waterways in the Central Valley

Prepared for:

Central Valley Regional Water Quality Control Board
11020 Sun Center Drive #200
Rancho Cordova, CA 95670-6114
Chris Foe
Project Manager

Prepared by

Victor de Vlaming
School of Veterinary Medicine: APC
1321 Haring Hall
University of California, Davis

Background

The production of fish that are safe for human and wildlife consumption is a beneficial use of aquatic resources in the Central Valley and Delta Estuary. Concentrations of mercury and other contaminants in fish collected in the Central Valley and Delta Estuary have been at levels that warrant concern for human and wildlife health. Data on fish tissue contamination by organic chemicals are not as extensive as for mercury, but recent publications (Larry Walker Associates, 2001, 2002, 2003; Lee and Jones-Lee, 2002; Greenfield et al., 2004) summarized data that showed concentrations of organochlorine (OC) pesticides and/or polychlorinated biphenyls (PCBs) in fish collected in some Central Valley and Delta Estuary waterways exceeded thresholds for human health. Consequently, fish consumption advisories related to these organic contaminants have been issued by the California Office of Environmental Health Hazard Assessment (OEHHA) for some of these Central Valley and Delta Estuary waterbodies. As a result of excess OC pesticide or PCB contamination of fish tissue 11 Central Valley or Delta Estuary waterbodies have been placed on the Clean Water Act (CWA) §303d list of impaired waterbodies by the Central Valley Regional Water Quality Control Board (CVRWQCB).

Several large fish sampling projects have been undertaken recently (1998-2005) in the Central Valley and Delta Estuary with the focus on mercury contamination. Fish sampling was funded by CalFed, CVRWQCB, and the State Water Resources Control Board (SWRCB) Surface Water Ambient Monitoring Program (SWAMP). These samples have been analyzed for mercury. Some of the fish (1998-2003) also have been analyzed for OCs and PCBs. With funding from the Sacramento River Watershed Program (SRWP), Larry Walker Associates has selected fish collected during 2005 in the Sacramento River watershed for analysis of OCs and PCBs. Analyses of the SRWP samples and those selected for this project will be conducted at the California Department of Fish and Game Water Pollution Control Laboratory (DFG WPCL).

Objectives

The primary intent of the current project is to select and analyze (for OCs and PCBs) archived fish samples collected in 2000 through 2005 in the Sacramento River watershed, San Joaquin River watershed and Delta Estuary. The primary objectives of this project include (1) Provide additional data to assist the CVRWQCB assess contamination in fish collected from waterbodies on the CWA §303d list (i.e., assist in decisions on listing, delisting, or continuing listing—see Table 1); (2) Provide data to assist OEHHA in determining whether fish from Central Valley and Delta Estuary waterways are safe for human consumption and in developing fish consumption advisories; (3) Provide data that will contribute to the analysis of fish contamination temporal trends (i.e., for determining or predicting when it will be safe to eat fish for these waterbodies and in deliberations regarding remediation); (4) Provide data that will contribute to assessment of the spatial distribution and extent of fish contamination in Central Valley and Delta Estuary waterways; (5) Provide data that will contribute to assessments of whether contamination

levels are safe for wildlife; and (6) Provide data for assessing whether 'bridging' among fish species is possible (i.e., Can level of contamination in several species be predicted from contamination in key species?). Entities contributing to this project are summarized in Table 2.

Selection of Sampling Sites

As stated above, all fish samples to be analyzed for OCs and PCBs in this project were originally sampled for mercury contamination projects. The rationale for selecting those sites is summarized in a QAPP prepared by Larry Walker Associates (Larry Walker Associates, 2006). Sites sampled for this project are listed in Table 3. Fish from a subset of those sites will be selected for OC and PCB analyses for the current project. The criteria for selecting sites for fish analysis are: (1) They are on waterways appearing on the CWA §303d list of impaired (consequent to OC or PCB fish contamination) waterbodies in the San Joaquin River watershed or Delta; (2) They were recommended by OEHHA; (3) They are sites with historical data on fish contamination and, thus, will contribute to the analysis of fish contamination temporal trends; (4) They will expand spatial coverage and, thus, contribute to assessment of the spatial distribution and extent of fish contamination in Central Valley and Delta Estuary waterways; and/or (5) They are sites where a large number of fish species were collected and, thus, provide data for assessing whether 'bridging' among fish species is possible.

Fish Sampling, Sample Transport, and Sample Storage Procedures

DFG's Moss Landing Marine Laboratory (MLML) was responsible for all fish sampling. Fish sampling, sample transport, and sample storage procedures are described in the Sacramento River Watershed Program QAPP (Larry Walker Associates, 2006) and appended documents. Sample custody and documentation procedures also are thoroughly described in that QAPP. See Attachment A for list of QAPPs and SOPs associated with this project.

Selection of Species to be Analyzed

A range of species was collected at the different sites. Largemouth bass was the key species for investigation of mercury contamination. For the current project white catfish and Sacramento suckers are the favored species for analyses because they are fatty bottom fish that tend to accumulate the contaminants of concern to a much greater extent than less fatty pelagic fish. The Sacramento River Watershed Program will be analyzing Sacramento suckers collected in the Sacramento River watershed during 2005. Thus, the Sacramento sucker data from the San Joaquin watershed and Delta can be directly compared to those collected in the Sacramento River watershed. This will aid in gaining an overall picture of contamination in the Central Valley and in assessing spatial

variation in this region. While bottom dwelling fatty white catfish, channel catfish, and Sacramento suckers tend to bioaccumulate the contaminants of interest to a much greater extent than less fatty pelagic fish, the ability to generally predict (i.e., bridge among species) contaminant burdens in pelagic fish based on data collected from the more fatty fish would be very valuable. At some sites sampled during 2005 for the mercury projects several species of fish were collected. At the sites where several species were collected composites will be prepared for all species where an adequate number of fish and tissue are available. Results of these analyses should provide data for assessing whether 'bridging' among fish species is possible (i.e., Can level of contamination in several species be predicted from contamination in key species?).

Compositing of Fish Samples

All samples to be analyzed for OCs and PCBs will be composited from three to five fish (see OEHHA, 2005). Compositing of samples will be performed at the DFG MPSL. Preparation of the filets from which the samples will be taken and the compositing procedures are described in the Sacramento River Watershed Program QAPP (Larry Walker Associates, 2006) and appended documents. See Attachment A for a list of QAPPs and SOPs associated with this project. At sites where a sufficient number of a species of interest were collected we intend to have as many composite samples as possible. For some of the analyses (e.g., temporal and spatial variation) we intend to conduct, it is important to have an estimate of variability of contamination in species of interest at the sites. Therefore, the average of fish size (standard length) in the different composites should be as equivalent as possible. While OEHHA recommends that composite samples should be consistent with the '75 percent rule' (the smallest fish contributing to the composite should have a standard length no less that 75 percent of the largest fish), our interest in variability in contaminant residues in fish of equivalent average size will take precedent over the '75 percent rule'. In a high percentage of the composite samples we select for analysis the '75 percent rule' will apply, but not in all.

Analytical Procedures

All fish composite analyses will be conducted at the DFG WPCL. Analytical procedures, detection and reporting limits, and QA measures are thoroughly described in the Sacramento River Watershed Program QAPP (Larry Walker Associates, 2006) and appendices. See Attachment A for list of QAPPs and SOPs associated with this project. Tables 4a and b provides a list of analytes to be measured in this project.

Quality Assurance

A QAPP will be prepared for this project that is consistent with the US EPA 24 Element QAPP Guidelines (US EPA, 1998) and the SWAMP Quality Assurance Management Plan (QAMP). See Attachment A for list of QAPPs and SOPs associated with this project.

Data Management

All data generated by this project will be maintained as described in the SWAMP data management Standard Operating Procedures (SOPs) and the project QAPP. DFG MLML is responsible for collection of all fish. The DFG WPCL is responsible for analytical chemistry data.

Data Analysis and Assessment

To predict whether fish are safe for human consumption tissue residues of OCs and PCBs will be compared to OEHHA's screening levels and guidance tissue levels (OEHHA, 2006). To predict whether OCs and PCBs are impacting wildlife, tissue residues will be compared to adverse effect concentrations reported in the science literature. Various statistical procedures (e.g., analysis of variance, regression analysis, etc.) will be used to assess spatial and temporal variation in fish contamination.

Reporting

Data generated in this project will be transferred to, and be electronically available from, the SWAMP database by DFG WPCL. An interpretive assessment report, that includes a literature review, will be prepared. This report will include an evaluation of potential threat of OC and PCB fish contamination to human and wildlife health.

Target Audience

The target audiences for the final report are the regulatory agencies charged with protecting beneficial uses of water resources, human health, and wildlife health (e.g., SWRCB, Central Valley Regional Water Quality Control Board, OEHHA, DFG, and US EPA).

Project Timeline

Item		Activity and/or Deliverable	Deliverable Due Date
1		**Contracts**	
		Subcontract Development	
2		**Quality Assurance Project Plan & Monitoring Plan**	
	2.1	Monitoring Plan	July 2006
	2.2	Draft Quality Assurance Project Plan	July 2006
	2.3	Final Quality Assurance Project Plan	September 2006
3		**Sample Selection and Chemical Analysis**	
	3.1	Selection of Tissue for Analysis	June 2006
	3.2	Chemical Analysis	January 2007
4		**Interpretive Report**	
	4.1	Draft Final Report	March 2007
	4.2	Final Report	June 2007

References

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Larry Walker Associates. 2003. Sacramento River Annual Monitoring Report: 2002-2003. Sacramento River Watershed Program. http://www.sacriver.org/subcommittees/monitoring/documents/SRWP_AMR_FINAL_070904.pdf

Larry Walker Associates. 2006. Quality Assurance Project Plan (QAPP), Revision 1.2.0: Sacramento River Watershed Program Monitoring for 2005-2007. Sacramento River Watershed Program.

Lee GF, Jones-Lee A. 2002. Organochlorine pesticide, PCB and dioxine/furan excessive bioaccumulation management guidance. G. Fred Lee & Associates, California Water Institute Report TP 02-06 to the California Water Resources Control board/Central Valley Regional Water Quality control Board. http://www.gfredlee.com/Unreliability.of.NAS.Criteria.pdf

OEHHA. 2005. General Protocol for Sport Fish Sampling and Analysis. Office of Environmental Health Hazard Assessment. http://www.oehha.ca.gov/fish/pdf/fishsampling041906.pdf

OEHHA. 2006. Development of Guidance Tissue Levels and Screening Values for common Contaminants in California Sport Fish: chlordane, DDTs, Dieldrin, Methylmercury, PCBs, Selenium, and Toxaphene. Office of Environmental Health Hazard Assessment. http://www.oehha.ca.gov/fish/gtlsv/pdf/draftgtlsvchddt.pdf

US EPA. 1998. Guidance for Quality Assurance Project Plans (QA/G-5). EPA 600/R-99/064. Office of Research and Development. Washington, DC.

Table 1. Waterways sampled in this project that are on the Central Valley Regional Water Quality Control Board's Clean Water Act §303(d) list due to organochlorine pesticides or PCB contamination.

Waterway	Listed for
Colusa Basin Drain	Group A pesticides
Lower Feather River	Group A pesticides
Natomas East Main Drainage	PCBs
Lower San Joaquin River	DDTs, Group A pesticides
Lower Merced River	Group A pesticides
Lower Tuolumne River	Group A pesticides
Lower Stanislaus River	Group A pesticides
Delta waterways (eastern portion)	DDTs, Group A pesticides
Delta waterways (western portion)	DDTs, Group A pesticides
Delta waterways (northern portion)*	DDTs, PCBs
Delta waterways (southern portion)*	DDTs

*Suggested for 303d listing.

Table 2. Summary of Sacramento and San Joaquin River Watershed and Delta SWAMP OC/PCB fish tissue project funding sources and responsible entities.

Funding Source	Amount	Responsible Entity	Tasks to be Completed by Responsible Entity
Delta Keeper	$20K	MLML/DFG	Fish collection/analyses
04/05 SWAMP Bioaccumulation	$53K	MLML/DFG	Fish collection/analyses
Sacramento River Watershed Program	~$50K	MLML/DFG	Fish collection/analyses
05/06 SWAMP Region 5 – LSAC	$48K	UCD	Final assessment report QAPP Monitoring plan
06/07 SWAMP Bioaccumulation			Under discussion

Table 3. Sites Sampled for Sacramento and San Joaquin River Watersheds and Delta SWAMP OC/PCB fish tissue project.

Watershed	Site Name	GIS Latitude	GIS Longitude
Sac River	American River @ Discovery Park	38.60094	-121.50550
Sac River	American River @ Nimbus Dam	38.68273	-121.17512
Sac River	Bear River d/s Wheatland	38.99626	-121.42191
Sac River	Colusa Basin Drain @ Rd 99E	38.81190	-121.77380
Sac River	Feather River @ Gridley	39.36549	-121.64545
Sac River	Feather River @ Nicolaus	38.89746	-121.59050
Sac River	Sacramento River @ Bend Bridge	40.25545	-122.22656
Sac River	Sacramento River @ Butte City	39.45680	-121.99534
Sac River	Sacramento River @ Colusa	39.13471	-121.93889
Sac River	Sacramento River @ RM44	38.43480	-121.52330
Sac River	Sacramento River @ Hamilton City	39.75150	-121.99749
Sac River	Sacramento River @ Ord Bend	39.62836	-121.99236
Sac River	Sacramento River @ Woodson Bridge	39.91273	-122.09313
Sac River	Sacramento Slough @ Karnak	37.88439	-121.65232
Sac River	Yuba River @ Marysville	39.16607	-121.55290
Sac River	Clear Creek	40.50563	-122.36662
Sac River	Sacramento River at Veterans Bridge	38.67506	-121.62860
Sac River	American River @ Goethe Park	38.60116	-121.32850
Sac River	Sacramento River @ Grimes	39.04619	-121.83951
Delta	Cosumnes River u/s I-5	38.25464	-121.40957
Delta	Middle River @ Bullfrog	37.93739	-121.53060
Delta	Middle River @ Tracy Blvd.	37.80355	-121.44653
Delta	Prospect Slough (mid-Prospect)	38.26284	-121.67150
Delta	Sacramento River @ Rio Vista	38.15427	-121.68859
Delta	Frank's Tract	38.04182	-121.62649
Delta	Liberty Island	38.31110	-121.66730
Delta	San Joaquin River @ Potato Slough	38.08784	-121.52031
Delta	San Joaquin River @ Mossdale	37.79239	-121.31161
Delta	Calaveras River off Deep Water Channel	37.96649	-121.36825
Delta	Smith Canal	37.96020	-121.33850
Delta	Paradise Cut	37.80021	-121.37002
Delta	Middle River @ Hwy 4	37.89104	-121.48879
Delta	Mildred Island	37.98330	-121.52730
Delta	Clifton Court Forebay	37.83110	-121.59006

(Continued)

Table 3. Continued

Watershed	Site Name	GIS Latitude	GIS Longitude
Delta	Whiskey Slough	37.96417	-121.46522
Delta	Sand Mound Slough	38.00830	-121.62250
Delta	Honker Cut @ 8-Mile Rd	38.06050	-121.45828
Delta	Taylor Slough	38.02844	-121.66628
Delta	Lost Slough (off Cosumnes River)	38.26714	-121.43847
Delta	Cosumnes River @ Hwy 99	38.35929	-121.34253
Delta	Beaver Slough (off S Fork Mokelumne River)	38.20393	-121.44740
Delta	Mokelumne River below Camanche Reservoir	38.21733	-121.05276
Delta	Camanche Reservoir	38.22560	-120.98029
SJ River	Merced River @ Hatfield State Park	37.35606	-120.96031
SJ River	Salt Slough @ Hwy 165	37.19189	-120.82478
SJ River	San Joaquin River @ Crows Landing	37.48125	-121.06520
SJ River	San Joaquin River @ Fremont Ford	37.30971	-120.93076
SJ River	San Joaquin River @ Patterson	37.49783	-121.08249
SJ River	San Joaquin River @ Vernalis	37.67130	-121.25920
SJ River	Stanislaus River @ Caswell State Park	37.69480	-121.20478
SJ River	Tuolumne River @ Shiloh Rd.	37.60315	-121.13162
SJ River	San Joaquin River @ Hwy 99	36.84256	-119.93306
SJ River	Mendota Pool/Mendota (Fresno) Slough	36.78584	-120.37166
SJ River	San Joaquin River at Laird Park (near J16 and Grayson Rd)	37.56132	-121.14727
SF Bay	Napa Marsh Complex Site 1		
SF Bay	Napa Marsh Complex Site 2		
SF Bay	Napa Marsh Complex Site 3		
SF Bay	Suisun Marsh	38.13430	-122.05950
	Big Break	38.01355	-121.72631
	Discovery Bay	37.91443	-121.60072
	Jenkinson Lake	38.71921	-120.56369
	Pardee Reservoir	38.25649	-120.84867
	Woodward Island	37.93869	-121.56067
	Middle Fork Cosumnes River	38.62466	-120.70222
	Millerton Lake	37.01828	-119.69930
	(New) Hogan Reservoir	38.16201	-120.79990
	Bear River b/w Feather River and HWY 99 (near Rio Oso)	38.96172	-121.54750

Table 4a. List of Analytes to be Measured – OCs.

Organochlorine Pesticides to be analyzed
Aldrin
Chlordane, cis-
Chlordane, trans-
Dacthal
DDD(o,p')
DDD(p,p')
DDE(o,p')
DDE(p,p')
DDMU(p,p')
DDT(o,p')
DDT(p,p')
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
HCH, alpha
HCH, beta
HCH, gamma
HCH, delta
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Methoxychlor
Mirex
Nonachlor, cis-
Nonachlor, trans-
Oxadiazon
Oxychlordane
Tedion
Toxaphene
Surrogates
PCB 207(Surrogate)
Dibromooctafluorobiphenyl(Surrogate)
DDD*(p,p')(Surrogate)
DBCE(Surrogate)

Table 4a. List of Analytes to be Measured – PCBs.

Polychlorinated Biphenyl (PCB) Congeners and Arochlor Compounds (by EPA Method 8082M)

PCB 008	PCB 138
PCB 015	PCB 149
PCB 018	PCB 151
PCB 027	PCB 153
PCB 028	PCB 156
PCB 029	PCB 157
PCB 031	PCB 158
PCB 033	PCB 170
PCB 044	PCB 174
PCB 049	PCB 177
PCB 052	PCB 180
PCB 056	PCB 183
PCB 060	PCB 187
PCB 066	PCB 189
PCB 070	PCB 194
PCB 074	PCB 195
PCB 087	PCB 200
PCB 095	PCB 201
PCB 097	PCB 203
PCB 099	PCB 206
PCB 101	PCB 209
PCB 105	**Surrogate (% Recovery)**
PCB 110	PCB 207(Surrogate)
PCB 114	**Calculated values from Lab**
PCB 118	PCB AROCLOR 1248
PCB 128	PCB AROCLOR 1254
PCB 137	PCB AROCLOR 1260

Attachment A: List of Referenced QAPPs and SOPs

De Vlaming, V. SWAMP Fish tissue analyses of organochlorine pesticides and PCB's in Central Valley surface waters. Prepared for CVRWQCB. 2006 (In Prep).

Larry Walker Associates. Sacramento River Watershed Program Monitoring for 2005-2007 QAPP. Revision 1.2.0. March 2006.

CDFG MPSL MLML Laboratory QAPP, Revision 5. February, 2006.

CDFG MLML SOP MPSL-102a Tissue Collection. February, 2005

CDFG MLML SOP MPSL-105 Tissue Preparation. February 2006

CDFG WPCL Laboratory QAPP, Revision 5. May, 2005.

CDFG MPSL SOP SO-TISS Analysis of Extractable Synthetic Organic Compunds in Tissue and Sediment (Organochlorine Pesticides, PCBs and PBDEs). Revision 9. March, 2005.