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SUBJECT: SUMMARY OF THE FINAL REPORT ENTITLED "PELAGIC ORGANISM DECLINE: ACUTE AND CHRONIC INVERTEBRATE AND FISH TOXICITY TESTING IN THE SACRAMENTO-SAN JOAQUIN DELTA"

This memorandum summarizes a final report entitled "Pelagic organism decline (POD): acute and chronic invertebrate and fish toxicity testing in the Sacramento-San Joaquin Delta." The study objective was to assess the role of chemical contaminants to the POD in the delta. It was conducted by the Aquatic Toxicology Laboratory at University of California, Davis and funded by the Interagency Ecological Program under the CALFED Bay-Delta Program in 2008-2010. The population decline of several pelagic fish species residing in the Sacramento-San Joaquin Delta has been scientifically documented and received public attention since 2004. However, it is unclear what might have caused the decline of the four critical fish species (viz., the endemic delta smelt, striped bass, longfin smelt and threadfin shad). Chemical contaminants, including pesticides commonly used in the delta, may be one of the factors that contribute to the POD.

The Department of Pesticide Regulation is interested in reviewing data that may show evidence of environmental impacts of pesticides in surface water. The study extensively examined water samples from 16 sites in the Sacramento-San Joaquin Delta for toxicity of commonly used pyrethroids and organophosphates.

The authors used six approaches to address the issues:

1. monitoring of water column toxicity using single-species tests with the amphipod *Hylella azteca*
2. laboratory toxicity tests of ambient samples using larval delta smelt *Hypomesus transpacificus*
3. *in situ* toxicity tests of ambient samples using fathead minnow *Pimephales promelas*, *H. azteca* and delta smelt
4. laboratory toxicity tests of ambient samples using copepods
5. determination of comparative sensitivity of select contaminants of model species and important resident species
6. development of sensitive biomarker tools for delta smelt and fathead minnow

The results were summarized for each of the approaches below.

1. Toxicity monitoring with *H. azteca*

The authors collected a total of 752 water samples on a biweekly sampling interval for 16 sites located in large delta channels and main-stem rivers from January 1, 2008 to December 31, 2009. Samples were tested for toxicity with a10 d *H. azteca* test. Survival and growth were reported as endpoints for acute and chronic toxicity, respectively (Table 1).

Piperonyl butoxide (PBO) is an enzyme inhibitor that synergizes pyrethroids but antagonizes organophosphases (OPs). Addition of PBO to the assay helps identify the source of toxicity. In this study, water samples that showed toxicity or significant PBO effects were subject to chemical analysis for 41 OPs and pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate/fenvalerate, fenpropathrin, lambda-cyhalothrin, and permethrin). Less than one percent of samples showed toxicity in acute, acute with PBO addition, and chronic tests without seasonal or geographic patterns (Table 1). With addition of PBO 13.3 percent (%) samples from 14 sites exhibited growth effects. The number of samples and pesticide detections are listed in Table 2. Pesticides with the highest concentrations exceeding invertebrate acute or chronic aquatic life benchmarks are bifenthrin, chlorpyrifos, and disulfoton. Aquatic life benchmarks, developed by the Office of Pesticide Programs based on risk assessments, are estimates of pesticide concentrations below which impacts to specific aquatic organisms are unlikely to occur <http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm#benchmarks>. Approximately 60% analyzed samples resulted in no detection of chemicals. The authors suspected that the high percentage of nondetects may be partly due to the high sensitivity of *H. azteca* to pyrethroid insecticides and relatively high detection limit of the analytical method. Toxic concentrations of some pyrethroids are lower than or close to the reporting and detection limits of the chemical analysis. Chemical degradation between time of sample collection and chemical analysis may have also contributed to the observed non-detects.

Table 1. Numbers and percentages of water samples toxic to *Hyalella azteca* in 752 samples collected from January 1, 2008 to December 31, 2009 in the Delta

Toxicity	Site	N	%
Acute	4	4	0.5
Acute with PBO	5	7	0.9
Chronic	6	7	0.9
Chronic with PBO	14	100	13.3

Table 2. Maximum concentrations of pesticides detected in 113 water samples that showed toxicity to *Hyalella azteca*

Category	Number of samples with detection	Percent of samples with detection	Chemical	OPP invertebrate benchmark Acute/chronic (ng/L)	Maximum Concentration (ng/L)
Pyrethroid	24	21	Bifenthrin	800/1.3	117
			Cyfluthrin	N/A	20
			λ-cyhalothrin	N/A	1.5
			Cypermethrin	210/69	16
			Esfenvalerate	25/17	9
			Permethrin	N/A	35
OP	13	12	Chlorpyrifos	50/40	78
			Diazinon	105/170	12
			Disulfoton	1950/10	17
Herbicide	10	9	Diuron	80,000/160,000	86

2. Toxicity monitoring with delta smelt
Water samples collected from 6 sites in March-May, 2008-2009 were tested with larval delta smelt for 7 days. The results are less conclusive in regard to toxic contaminants because other environmental stressors such as turbidity, salinity and electrical conductivity (EC) are important factors that can influence larval delta smelt survival. Nevertheless, the report concluded that the water quality in the Sacramento River at Hood, in the San Joaquin River at Rough and Ready Island, and near the confluence of Cache and Lindsey Sloughs was at times unfavorable to larval delta smelt.

3. *In situ* monitoring with larval delta smelt, larval fathead minnow and *H. azteca*
96-h and 7-d exposures were conducted during March-May 2009. No toxicity to *H. azteca* or fathead minnow was observed. Larval delta smelt survived poorly in both the control and ambient water.

4. Toxicity monitoring with copepods
One 7-d toxicity pilot test was conducted with juvenile *E. affinis*. The copepod survival rates were poor (<50%) both in controls of various ECs and three ambient waters. A control with an EC value 1930 µs/cm resulted in a survival of 90%, suggesting that ECs can significantly affect copepod survival. Poor control survival indicates that the 7-d toxicity testing standard for copepods has not yet been well established.

5. Comparative species sensitivity

Species sensitivity to organophosphates (chlorpyrifos, diazinon), pyrethroids (bifenthrin, cyfluthrin and permethrin), copper and ammonia were assessed between fish (delta smelt and fathead minnow) and among invertebrates (*H. azteca, C. dubia,* and copepod *E. affinis*) by using 96-h LC_{50} values. The results indicate that larval delta smelt wwa 1.8 to >11-fold more sensitive than larval fathead minnow to all the tested chemicals with the exception of permethrin. In invertebrates, *H. azteca* was most sensitive to pyrethroids, *C. dubia* was most sensitive to organophosphates (chlorpyrifos, diazinon). *E. affinis* was most sensitive to ammonia/um but least sensitive to organophosphates. It is unclear which species, *C. dubia* or *E. affinis,* is more sensitive to copper, un-ionized ammonia and pyrethroids because of the discrepancies of LC_{50} values reported by the University of California, Davis (UCD) Aquatic Toxicity Laboratory and Dr. Teh's Laboratory.

E. affinis 96-h LC_{50} values from the two UCD laboratories were also compared to the endpoints of other standard toxicity tests including LC_{50} and growth (EC_{25}) of *H. azteca* 10-d test, LC_{50} of *C. dubia* 96-h test and reproduction (EC_{25}) of *C. dubia* 7-d test. The results indicate that *H. azteca* 10-d LC_{50} and growth were the most sensitive endpoints for pyrethroids, and C. dubia 96-h LC_{50} and 7-d reproduction were the most sensitive endpoints for OPs (chlorpyrifos and diazinon) and copper. The results suggest that the endpoints of standard toxicity tests (10-d *hyalella* test, and 96-h and 7-d *C. dubia* tests) are protective of the copepod species in assessing OP and pyrethroid pesticide contamination in the delta.

UCD Aquatic Toxicity Laboratory also evaluated the suitability of the 10-d *Hyalella* test for chronic water column toxicity testing in comparison with the 7-d *C. dubia* test. Similar results discussed in the previous paragraph were reported on the species sensitivity to pyrethroids and OPs. Since *Hyalella* can tolerate a broader range of conductivity compared to *C. dubia*, the species can be a valuable surrogate test species for evaluating some California inland water bodies where the conductivities exceed the tolerant levels of *C. dubia*. The report concludes that *H. azteca* is a viable test species for evaluating ecosystem health, especially when the conductivity range of samples falls between 200 and 10,000 µs/cm, and pyrethroids may be present in the sample.

6. Sublethal indicators of contaminant effects

Seven studies were conducted to identify molecular biomarkers for delta smelt exposed to esfenvalerate, copper and ammonia, for striped bass exposed to PAH, and for fathead minnow exposed to bifenthrin and fipronil. Swimming performance, cDNA microarray and Cytochrome P450 induction were the tools applied to evaluate the exposures of various toxicants in sublethal concentrations. Generally, the biomarker expressions are rather complex. A suite of biomarker genes can respond rapidly to chemical exposures in various fish. For instance, esfenvalerate could affect genes associated with immune responses, apoptosis, redox osmotic stress, detoxification, and growth and development in larval delta smelt. Bifenthrin at 0.07 µg/L and fipronil at 53 µg/L could induce stress-related gene expression. The study demonstrated that biomarker gene profiles responded to the two chemicals could be clustered and distinguished in most cases. Overall, those studies demonstrate that molecular biomarkers hold significant promises as screening tools for identification of pesticide contaminations in the field. However, it remains a challenge for the molecule biomarker tools to provide conclusive evidence of contaminant impacts on fish species in field monitoring.