CENTRAL COAST REGION CONDITIONAL WAIVER COOPERATIVE MONITORING PROGRAM

FOLLOW-UP MONITORING REPORT:

PESTICIDES AND TOXICITY TO *HYALELLA AZTECA* IN SEDIMENTS

2010

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"Managing the Cooperative Monitoring Program on Behalf of Ag"

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Executive Summary

In May 2010 benthic sediment samples from 46 Cooperative Monitoring Program (CMP) sites were collected and analyzed for organochlorine (OC), pyrethroid, and organophosphate (OP) pesticides and were tested for toxicity to the macroinvertebrate, *Hyalella azteca*. Four additional sites were planned for this monitoring event, however these were dry and could not be sampled. All samples were analyzed concurrently with regularly scheduled monitoring of other water quality parameters (Table 1). Watersheds monitored (including tributaries) included the Pajaro River, Lower Salinas River, Salinas Reclamation Canal, creeks tributary to Estero Bay (San Luis Obispo), Santa Maria River, Oso Flaco Creek, Santa Ynez River, and South Coast creeks tributary to the Pacific Ocean (Santa Barbara; Table 2).

Between May 24 and May 26, 2010, sediment samples were collected from each site for laboratory analysis of 31 OC, 12 pyrethroid, and 1 OP pesticide (Table 3). Organochlorine and OP compounds were measured by gas chromatography/mass spectrometry (EPA 8270Cm). Pyrethroid compounds were measured by gas chromatography/mass spectrometry with negative chemical ionization (NCI-GCMS). Sediment samples were also collected for laboratory tests of toxicity to the benthic invertebrate, *H. azteca*, and results were analyzed for statistically significant differences in survival and growth compared with non-toxic control sediments.

Organochlorines were detected at 40 sites, pyrethroids at 31 sites and chlorpyrifos at 21 of the sites monitored (Tables 4-6). Zero pesticides were detected at 5 sites, whereas the highest number of unique pesticides detected at a single site was 24. Of the 31 OCs analyzed, the compounds 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, cis-chlordane, cis-nonachlor, DCPA, dicofol, dieldrin, endrin, heptachlor, perthane, toxaphene, trans-chlordane and trans-nonachlor were detected at one or more sites (Table 4). Of the 12 pyrethroids analyzed, the compounds allethrin, bifenthrin, cyfluthrin, cypermethrin, danitol (fenpropathrin), esfenvalerate, fenvalerate, fluvalinate, lambda-cyhalothrin, and permethrin were detected at one or more sites (Table 5). The only OP analyzed, chlorpyrifos, was detected at 46% of sites. Detection of multiple pesticide compounds in sediment from the same site was common, as 54% of sites where pesticides were detected had 10 or more in combination. The detection of a single pesticide at a site was uncommon and occurred only at 4 sites where only a breakdown product of DDT was detected.

Survival rates for *H. azteca* were significantly lower in sample sediments than in control sediment from 27 of the 46 sites sampled (59% of sites). Survival based toxicity was observed at one or more sites in all areas monitored except Santa Ynez. Survival based toxicity in Santa Maria was observed at 100% of sites monitored with 0% survival at 6 of the 9 sites sampled (67% of sites). The Upper Pajaro watershed, Lower Pajaro, Salinas mainstem, Salinas tributaries and drains, Santa Barbara coastal streams and San Luis Obispo areas also showed significant survival effects to *H. azteca*, at 17%, 50%, 50%, 83%, 50% and 25% of sites, respectively. Pesticides were detected in 26 of the 27 sites that demonstrated toxicity to invertebrate survival, although sometimes at low concentrations below the threshold of 0.5 Toxic Units (TUs) generally associated with toxic effects (Weston et al. 2004). Survival rates at sites showing significant mortality effects ranged from 0% to 91% of survival in control sediments. Toxic effects to growth could only be analyzed statistically in samples where there was not a significant effect on survival, and only 1such sample tested showed evidence of growth-related effects.

Although OC pesticides were the most commonly detected and widespread class found in this study (detected at 87% of sites), their concentrations were too low to likely make a substantial contribution to toxicity. Added OC concentrations summed to less than 0.1 TU at all sites. Chlorpyrifos and pyrethroid pesticide concentrations were more likely contributors to toxicity. In all cases where toxic units of an individual pesticide were greater than 0.5 TUs in sediment, significant mortality was observed; and 70% of sites with significant mortality had at least one pesticide present in concentrations greater than or equal to 0.5 TUs. Chlorpyrifos and added TUs of pyrethroids were detected at levels greater than 0.5 TUs at 30% and 46% of sites sampled respectively.

Table of Contents

List of Tables & Figures

1 INTRODUCTION

The Cooperative Monitoring Program (CMP) began monthly surface water monitoring at 25 sites in the Lower Salinas and Santa Maria watersheds in January 2005. Monthly monitoring of these 25 sites in 2005 completed Phase I of the CMP. In January 2006, Phase II began with monthly surface water sampling at original sites plus 25 additional sites in the following areas: the Pajaro River and tributaries, creeks in San Luis Obispo County (tributaries to Estero Bay and the Pacific Ocean), the lower Santa Ynez River, and South Coast creeks (near Santa Barbara, tributaries to the Pacific Ocean). The CMP measures basic physical and chemical water quality parameters, as well as in-stream flows and nutrient-related parameters (Table 1). Water column toxicity to invertebrates, fish, and algae is measured 4 times per year, and sediment toxicity to invertebrates is measured once a year. Water column monitoring for organophosphate (OP) pesticides has been performed on several occasions by the CMP, as special "Follow-up Monitoring" projects (CCWQP 2008, CCWQP 2009, CCWQP 2010b). The May 2010 monitoring discussed in this report involved the first analysis of pesticides in benthic sediments, along with sediment toxicity to invertebrates, and included both Phase I and Phase II sites.

Water quality issues in the Central Coast region of California include impairment of drinking water sources, contact recreation, and aquatic life beneficial use, based on water quality objectives (WQO's) established by the Central Coast Regional Water Quality Control Board (CCRWQCB). Pesticides are generally not found at levels harmful to humans, however impacts to aquatic life include possible threats to endangered and threatened species found in this region, including both the red-legged frog (*Rana aurora draytonii*) and the steelhead trout (*Onchorhyncus mykiss*). All mainstem rivers and several creeks within the CMP monitoring area have documented populations of steelhead trout (*Onchorhyncus mykiss*; Moyle et al. 2008). Pesticides have been shown to not only effect the survival, growth and reproductive health of individual species, but also to affect the community structure, abundance and diversity of macroinvertebrates in stream systems (Anderson et al. 2003a). Reduction of macroinvertebrate populations, a food source for higher species such as fish and frogs, affects multiple parts of the food web. Furthermore, the rivers of the Central Coast flow into the Pacific Ocean and estuaries, where marine life can be affected by and/or bioaccumulate pesticides and toxicants (Anderson et al. 2007).

Most watersheds in the CMP monitoring area incorporate mixed land uses, with agricultural land use present to varying degrees and intensity. Synthetic pyrethroids and OP compounds are applied to crops grown in CMP monitoring areas, and pyrethroids are also used in urban areas for structural pest control, landscape maintenance and pet grooming. Monitoring both water and sediment is important for detecting pesticides in waterways because some pesticides remain dissolved in the water column while others adhere to particles. Sorbed pesticides can either remain suspended in the water column or settle out in bed sediment. In general, synthetic pyrethroids tend to be more prevalent in sediments because of their hydrophobic properties and tendency to adsorb to particles, whereas OP pesticides are more water soluble and therefore likely to be found in the water column (Hunt et al. 2006). The OP chlorpyrifos in particular tends to be an exception to this, with a higher tendency to sorb to sediments than most other OP's. The CMP has previously monitored OPs in sample water from all CMP sites. To address Ag Waiver requirements for "Follow-up" monitoring and further explore the link between pesticides detected in sediments and toxicity, pesticides in sediments were measured in the Phase I & II monitoring areas concurrently with regularly scheduled CMP water quality and sediment monitoring in May 2010.

Many of the 25 Phase I sites have shown repeated toxicity to aquatic invertebrates in the water column (CCWQP 2008; CCWQP 2009a); however there have been fewer studies of the toxicity of pesticides adhered to bed sediments in waterbodies in this region, and no such studies to date by the CMP. Sediment based toxicity monitoring is becoming increasingly relevant as pyrethroid use increases for agricultural pest control and in urban areas, where high concentrations are found in commercial and residential dominated landscapes (Weston et al. 2004, Amweg 2005). Legacy organochlorine (OC)

pesticides also tend to adhere to sediments and, in general, are more likely to be found in sediments than in the water column (Weston et al. 2004). Increased regulation of OP materials due to negative health and environmental impacts along with increased pest resistance to these compounds has resulted in declining use since 1997, with the number of acres treated with OPs in California falling from about 12 million to under 4 million in 2009 (CA DPR 2010). Conversely, the use of some pyrethroid pesticides has increased in recent years (CA DPR 2008). Due to the high frequency of detection in California waterways at levels toxic to *H. azteca*, several pyrethroids were simultaneously placed under re-evaluation by the California Department of Pesticide Regulation (CA DPR) on August 31, 2006 (CA DPR 2008). Earlier studies indicate the presence of OCs and pyrethroids in Salinas and Pajaro River sediments at concentrations shown to cause biological harm (Kozlowski et al. 2002, Starner and Kelley 2004, Hunt et al 2006). Hunt et al. (2006) analyzed sediments from several waterbodies in the Salinas and Pajaro watersheds in May 2002 and detected DDT, DDE, dieldrin and endrin (OCs) in concentrations above the Threshold Effects Concentration, and measured lambda-cyhalothrin in Alisal Creek at twice the median lethal concentration (LC_{50}) value. The CA DPR reported a detection frequency of 60% for pyrethroids in the Salinas area, with 20% of sites having more than 1 TU of added pyrethroid concentrations (Starner and Kelly 2004). The CMP Follow-up monitoring study discussed in this report examines the extent and concentration of these pesticides in CMP waterbodies, in relation to patterns of toxicity to benthic macroinvertebrates.

In this study, measured pesticide concentrations were compared with observed toxicity to the invertebrate, *H. azteca*, in concurrently collected sediment samples. Data were analyzed to examine relationships between pesticide concentrations and toxic units (TUs) and survival rates for *H. azteca* in standardized toxicity tests.

To date the focus of California state regulatory boards has largely been on pesticide concentrations in water. The Central Coast Regional Water Quality Control Board's (CCRWQCB's) "303d-listing" criteria for the protection of aquatic life do not address pesticides in sediments (CCRWQCB 2009). Although the use of pyrethroids began in the 1980s, there is still limited data available on their prevalence and concentrations in regional waterways or on their potential to affect life in streams and the ecology of these systems.

When reading this report, it is important to note that this study addressed only one of many potential sources of sediment toxicity – pesticides – and was observational, rather than experimental in nature. Thus only an associative and not a *causal* relationship between the pesticide concentrations and toxicity observed can be statistically confirmed from these data alone. Further study would be required to rule out other sources of toxicity (e.g. metals), or to establish a causal link between pesticides found and observed toxic effects. For this purpose, Toxicity Identification Evaluations (TIEs) have been used by researchers to identify causes of toxicity when multiple toxicants are present, including distinguishing between the effects of pyrethroids, OPs and metals (Phillips et al. 2007).

2 METHODS

2.1 Monitoring Approach & Sites

The purpose of this study was to characterize pesticide concentrations in bed sediments and identify sediment toxicity to invertebrates within the Pajaro River, Moro Cojo, Salinas River and Reclamation Canal, Estero Bay, Santa Maria River, Santa Ynez River, and South Coast hydrologic units (HUs). Selection of waterbodies for the broader CMP was conducted in 2004 and based on several criteria, including:

- Waterbodies which are on the Clean Water Act 303(d) list of impaired waterbodies for pollutants associated with irrigated agriculture;
- Waterbodies which have evidence of serious nitrate groundwater contamination in areas associated with intensive agricultural activity; and
- Waterbodies with documented beneficial use impairment(s) from pollutants associated with irrigated agriculture and which are proposed for future placement on the 303(d) list.

Monitoring sites on these waterbodies were selected for public access and to best characterize agricultural inputs, and are generally located along the mainstem and at the lower ends of tributaries in areas associated with agricultural activity. In a few cases, sites were also located to aid in distinguishing agricultural inputs from other sources (e.g., industrial, urban, etc.). Most sites were selected from the suite of existing monitoring sites from the CCRWQB's Central Coast Ambient Monitoring Program (CCAMP), for which at least one year of monitoring data were already available. For Follow-up studies, subsets of CMP sites are sometimes examined to focus resources on areas of most concern. For this study, all 50 sites were included in the monitoring plan, because the presence of pesticides at sites both with and without a history of sediment toxicity was of interest.

Sediment samples for toxicity analyses are collected from CMP sites during the spring of each year. During May 2010, sediment samples were collected from all sites in each CMP hydrologic unit (HU), except at sites that were dry or ponded. The plan for monitoring included the following locations:

- 27 sites in the Northern Monitoring Unit
  - 10 sites in the Pajaro River HU, and
  - 17 sites in the Moro Cojo and Salinas River HUs, and
- 23 sites in the Southern Monitoring Unit
  - 6 sites in the Estero Bay HU,
  - 10 sites in the Santa Maria River HU (including Oso Flaco),
  - 3 sites in the Santa Ynez HU
  - 4 sites in the South Coast HU.

Site longitude and latitudes are provided in Table 2 and sites are described in greater detail in the CMP Quality Assurance Project Plan (CCWQP 2006).

To fulfill CMP Follow-Up Monitoring requirements in the Ag Waiver, additional sediment samples from each CMP site were collected and analyzed for organochlorine (OC), pyrethroid, and organophosphate (OP) pesticides. Total organic carbon (TOC) was also measured since it can affect the bioavailability of some hydrophobic pesticides (e.g. pyrethroids). Samples were also collected for sediment grain size and

percent solids analyses so as to characterize the physical properties of the sediments (e.g. sediments dominated by sand typically have low concentrations of hydrophobic pesticides).

2.2 Sample Collection Methods

Ambient sediment samples were collected for the various analyses as described in the CMP QAPP and in the 2010 QAPP amendment (Pacific EcoRisk Sediment Sampling SOP; CCAMP SOP; CCWQP 2006; CCWQP 2010).

Briefly, depositional (i.e. fine-grain) sediments were collected from the upper 2 cm of the streambed using a pre-cleaned stainless steel scoop and placed into a pre-cleaned stainless steel bowl. Once approximately 4 L of sediment had been collected and placed in the bowl, the sediment was thoroughly homogenized by manual stirring with a large stainless steel spoon, after which the homogenized sediment was partitioned into containers as described in Table A.

Table A. Characterization of CMP sediment samples.

Parameter	Sample Container	Sample Volume	Immediate Processing and Storage	Holding Time
Physical and Conventional Parameters				
TOC and percent solids	Glass	8 oz	Store at 0-6˚C	28 days
Grain size	Ziplock bag[b]	5 gm	Store at 0-6˚C (do not freeze)	6 months
Toxicity				
Sediment bioassays	Glass	2 Liters	Store at 0-6˚C (do not freeze)	14 days
Pesticides				
Pyrethroid	Glass	8 oz	Store at 0-6˚C	Extract within 14 days and analyze within 40 days
Organochlorine				
Chlorpyrifos				

a – TOC, percent solids, and pesticides are collected into the same 8-oz jar.
b – Lab prefers to have samples collected in ziplock bag instead of 125 mL glass jar.

Sample transportation and handling followed the guidelines in the CMP QAPP. Pacific EcoRisk performed the sediment toxicity analyses, grain size analysis was performed by ABC Labs in Torrance, CA and all remaining analyses were performed by CRG Marine Labs in Torrance, CA.

2.3 Analytical Methods

2.3.1 Organochlorine and organophosphate pesticide analysis

Organochlorine and OP compounds were measured by gas chromatography/mass spectrometry (EPA 8270Cm). Briefly, compounds were serially extracted from the sample solution with an organic solvent at high and low pH, separated using a gas chromatographic column, and quantified according to mass:charge ratio by a mass spectrometer. Analyte-specific method detection limits (MDL) ranged from 1 to 10 ng/g (ppb – parts per billion), with reporting limits (RLs) from 2 to 50 ng/g. The laboratory Standard Operating Procedure for this method is included in the 2010 QAPP amendment (CCWQP 2010a).

2.3.2 Pyrethroid pesticide analysis

Pyrethroid compounds were measured by gas chromatography/mass spectrometry with negative chemical ionization (NCI-GCMS). Briefly, compounds were serially extracted from the sample solution with an organic solvent at high and low pH and separated using a gas chromatographic column. Methane gas was then introduced into the mass spectrometer that caused a "soft ionization" of the molecules, which were quantified according to mass:charge ratio by a mass spectrometer. Analyte-specific MDLs ranged from 0.5 to 5 ng/g, with RLs from 2 to 25 ng/g (1). The laboratory Standard Operating Procedure for this method is included in the 2010 QAPP amendment (CCWQP 2010a).

2.3.3 Total organic carbon analysis

Total organic carbon (TOC) was measured by catalytic combustion (EPA 9060Am) that converted the sediment carbon compounds into carbon dioxide, which was then measured directly with an infrared detector. The amount of carbon dioxide detected is directly proportional to the amount of carbon in the sample. The MDL was 0.01% dry weight (DW) with a RL of 0.02% DW. The laboratory Standard Operating Procedure for this method is included in the 2010 QAPP amendment (CCWQP 2010a).

2.3.4 Physical properties analysis

Percent solids were measured by a measured weight method (SM 2540B). Briefly, a measured mass of wet sediment was dried to a constant weight in a convection oven. The differences in weight between the wet and dried sediment was used to calculate the percent solids. The percent solids MDL was 0.10% DW, with a RL of 0.10% DW.

Grain size was measured by mixing the sediment with water and then determining the particle size distribution of the sample using a light scattering method (SM 2560D). The laboratory Standard Operating Procedures (SOPs) for this method and the percent solids analysis are included in the 2010 QAPP amendment (CCWQP 2010a).

2.3.5 Toxicity analysis

The sediment toxicity tests conformed to the US EPA guidelines "Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates" (EPA/600/R-99/064). The freshwater sediment toxicity test with *H. azteca* consists of exposing the organisms to sample sediments for 10 days, after which effects on survival and growth are evaluated. The sediments were tested at the 100% concentration (i.e., undiluted) only. The control treatment consisted of a composite of reference site sediments that have been maintained under culture at the PER lab for >3 months.

There were 8 replicates for each sediment tested, each replicate containing ~100 ml of sediment and clean overlying water (synthetic moderately hard water, modified for use with *H. azteca* as per the EPA test guidelines). The test replicates were prepared the day prior to test initiation and were placed in a temperature-controlled environment at 23˚C. The following day, immediately prior to test initiation, a small aliquot of the renewed overlying water was collected from each of the 8 replicates for each test and composited for measurement of "initial" water quality characteristics (pH, dissolved oxygen [D.O.], conductivity, alkalinity, hardness, and total ammonia). Each sediment test was then initiated with the random allocation of 10 *H. azteca* (7-14 days old, all within 2 days age of one another) were randomly allocated into each of 8 replicates.

During each of the following 9 days, each test replicate was examined for the presence of any dead amphipods. Upon observation, dead organisms were carefully removed from each replicate. A small aliquot of the overlying water in each of the 8 replicates was then collected and composited as before for measurement of "old" D.O., after which each replicate was flushed with one volume of fresh water. Another small aliquot of the overlying water in each of the 8 replicates was then collected and composited as before for measurement of "new" D.O., after which each replicate was fed 1.5 mL of Yeast-Cerophyll®-Trout Chow food prepared by PER following the protocol in "Short-term methods for estimating the chronic toxicity of effluents and receiving waters to marine and estuarine organisms" (EPA/821/R-02/013 2002).

After 10 days exposure, an aliquot of overlying water was collected from each replicate and composited for analysis of the "final" water quality characteristics. The sediments in each replicate container were then carefully sorted and sieved and the number of surviving organisms determined. The surviving organisms were euthanized in methanol, rinsed in de-ionized water, and transferred to small pre-weighed weighing pans, which were placed into a drying oven at 100˚C. After drying for ~24 hrs, the pans were transferred to a desiccator to cool, and then weighed to the nearest 0.01 mg to determine the mean dry weight per surviving organism for each replicate. The resulting survival and growth (mean dry weight) data were then analyzed relative to control performance to evaluate any toxic effects due to the sediments. All statistical analyses were performed using the CETIS® statistical software. In concept, survival and growth rates for *H. azteca* in the test replicates were compared statistically to rates from the control samples. Sediments that show a significant difference between test and control performance were deemed toxic. In addition to determination of "significant toxic effect," results were also expressed as the test samples' performance as a "% of control" samples' performance, where "% of control" is conceptually equal to $\frac{\text{Test sample survival or growth rate}}{\text{Control sample survival or growth rate}}$ x 100, with some additional calculations relative to replicate samples. Supporting documentation for toxicity testing procedures is provided in the CMP's QAPP (CCWQP 2006).

2.3.6 Calculating toxic units

Toxic units (TUs) provide a means to compare the relative toxicities of concentrations of different pesticides with one another and to express pesticide concentrations in terms of their expected toxic effects to aquatic organisms. Toxic units for pesticides (and other toxicants) in water were calculated by dividing the pesticide concentration by the LC_{50} value specific to the test organism's length of exposure. In sediments, a TU is the pesticide concentration in sediment normalized to total organic carbon (TOC) divided by the test organism-specific median lethal concentration (LC_{50}) over the test period. A TU of 1 represents an expected survival rate of 50% of the test organism over the test duration (i.e. *H. azteca* over 10 days). Pesticides or toxicants with a strong affinity for organic carbon tend to adhere to these particles and are less bioavailable and therefore generally less toxic to aquatic organisms when sediments have high TOC content (Nebeker et al. 1989). Toxic units of pesticides in sediments were based on LC_{50} values identified via a literature review (shown in Table 3) and calculated using the following equation:

$$TU = \frac{C}{LC_{50} * S}$$

where TU is dimensionless, C is the concentration of pesticide in sediment (ng/g), S is the concentration of TOC in sediment (g/g), and LC_{50} is the median lethal concentration (ng/g).

2.4 Quality Assurance and Quality Control

Sediment quality data collected by this monitoring program are compatible with State of California Surface Water Ambient Monitoring Program (SWAMP) data quality objectives. The CMP also generally follows informal guidance provided by the US EPA regarding data verification and validation.

Quality assurance protocols are described in detail in the QAPP (CCWQP 2006). Briefly, field blank and duplicate samples were collected regularly to identify any contamination and to demonstrate the precision of sampling procedures. Laboratory method blanks, duplicates, and matrix spikes were also analyzed to identify any contamination and to demonstrate precision and accuracy of analytical procedures. Additional details regarding quality control for toxicity tests are given in QAPP Appendix B (CCWQP 2006). Both field and laboratory instruments were calibrated according to a regular schedule and user manuals where applicable. Data generated by analytical laboratories were reviewed and qualified as necessary.

3 RESULTS

A total of 49 samples (including duplicates) were collected for sediment analysis of organochlorine (OC), organophosphate (OP) and pyrethroid pesticides as well as toxicity to *H. azteca* at 46 sites during 1 monitoring event in May 2010. Monitoring was planned for 50 sites, but the following 4 sites did not have flowing water during the monitoring event and samples were not taken: Gabilan Creek (309GAB), Los Berros Creek (310LBC), Davenport Creek (310SLD), and Santa Maria River at Highway 1 (312SMI). A total of 44 pesticides or pesticide breakdown products were analyzed. Classes of pesticides and breakdown products analyzed included 31 organochlorine (OC) pesticides, 12 pyrethroid pesticides and 1 organophosphate (OP) pesticide (Table 3). Most of the OC pesticides have been previously banned or severely restricted by the US EPA (with the exception of dicofol, DCPA, methoxychlor and endosulfan), so current detections usually indicate the presence of persistent legacy pesticides. Of the 44 pesticides and breakdown products analyzed, 16 were not detected at any sites and 28 were detected at one or more sites. The OC pesticides detected at one or more sites were 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, cis-chlordane, cis-nonachlor, DCPA, dicofol, dieldrin, endrin, heptachlor, perthane, toxaphene, trans-chlordane and trans-nonachlor. The pyrethroids detected were allethrin, bifenthrin, cyfluthrin, cypermethrin, danitol (fenpropathrin), esfenvalerate, fenvalerate, fluvalinate, lambda-cyhalothrin, and permethrin. The only OP analyzed, chlorpyrifos, was frequently detected (21 out of 46 sites).

Of the 46 sites sampled, at least 1 pesticide was detected at 41 sites; whereas no pesticides or breakdown products were detected in sediment at 5 sites. Tables 4 and 5 show the concentrations found at each site; Figures 1 through 3 show average concentrations of each compound by sub-region. In the NMU, the Salinas Reclamation Canal (309ALG & 309JON), Espinosa Slough (309ESP), and Tembladero Slough (309TEH) sites had detections of 21 or more different compounds. No pesticides were detected in sediment at the Tequisquita Slough (305TSR) or Miller's Canal (305FRA) in the upper Pajaro watershed, nor in the mainstem Salinas at Greenfield (309GRN) or Gonzalez (309SAG), although the *breakdown product* 4,4'-DDE was detected at both. In the SMU, 20 different compounds were detected in the Bradley Channel (312BCJ) and Main St. ditch (312MSD). No pesticides were detected in the Santa Ynez River, Chorro Creek, Bell Creek or Arroyo Paredon, although the breakdown product 4,4'-DDE was detected at the Santa Ynez River at 13th Street (314SYN).

Toxic units were calculated for each pesticide where literature values for the sediment LC_{50} could be found for the test organism (Table 3). For the pesticides and breakdown products where an LC_{50} was not available, the TU was not computed nor was any value added to the total TUs. The added TUs for each pesticide class are shown in Table 6 as is the addition of TUs across all classes of pesticides. It is always important to exercise caution in using total TUs as an indicator of toxic potential for reasons discussed further in Section 4 of this report (Discussion). Toxic units related to all pesticide classes were present at 34 sites, including more than 0.50 added TUs across all pesticide classes at 22 sites. Organochlorine concentrations were greater than 0.00 TUs at 19 of the sites sampled and the highest added OC TU was 0.09. Pyrethroid concentrations were at least 0.01 TUs at 30 sites and were at least 1.0 TU at 18 sites. The only OP pesticide tested, chlorpyrifos, was found in concentrations at least 0.01 TUs at 21 sites and greater than 1.0 TU at 6 sites. The TUs from individual pesticides (as opposed to the mixes just described) for each site are shown in Table 7; Figures 4 through 9 show TU's for each pesticide class by site, and Figure 10 gives invertebrate survival rates by site. Figure 11 displays a barplot by subregion of the number of sites with TUs greater than 0.5 for individual pesticides: chlorpyrifos (14 sites), bifenthrin (14 sites), cyfluthrin (3 sites), cypermethrin (7 sites), danitol (3 sites), esfenvalerate (2 sites), fenvalerate (1 site), lambda-cyhalothrin (12 sites), and permethrin (4 sites).

Survival/ mortality of *H. azteca* in sample sediments compared with control sediments showed significant mortality at 27 of the 46 sites monitored (Table 6) and growth was significantly affected at 1 additional site. In the NMU, 16 of 26 sites showed statistically significant effects to aquatic invertebrates in

sediment, 15 lethal effects and 1 growth related. In the SMU, 12 of 20 different sites showed significant effects to invertebrates, all of these lethal. Sites in Santa Ynez (3 out of 3) showed no evidence of toxic effects and in San Luis Obispo, 1 out of 6 sites showed significant mortality.

Survival rates for *H. azteca* were expressed as "percent of control," making it possible for sample sediment survival to numerically exceed 100% in some cases. The sites showing toxicity had survival rates ranging from 0% to 91%. The sites not showing toxicity had survival rates ranging from 85% to 105%.

3.1 Organochlorine Pesticides and Breakdown Product Results

Due to their environmental persistence, some legacy OC pesticides and their breakdown products were detected in sediments from many CMP sites during this study. Of the 31 OC pesticides and breakdown products analyzed, 17 were detected at 1 or more sites and 11 were detected at more than 20 sites. The OC compounds 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, cis-chlordane, cis-nonachlor, DCPA, dicofol, dieldrin, endrin, heptachlor, perthane, toxaphene, trans-chlordane and trans-nonachlor were detected at one or more sites. The following pesticides or byproducts were not detected at any of the sites monitored: aldrin, BHC (alpha, beta, delta and gamma), endosulfans (I, II and sulfate), endrin aldehyde and endrin ketone, heptachlor, methoxychlor, mirex, and oxychlordane. Of the OC pesticides still registered for use in California, DCPA was detected at 10 sites and dicofol at 20 sites, whereas endosulfans (I, II and sulfate) and methoxychlor were not detected at any sites. Despite the frequent detection of OCs (87% of sites sampled), their expected toxicity (added TUs where a sediment LC_{50} was available) was less than 0.10 TUs for *H. azteca* at all sites. Compared with the other two pesticide classes (OPs and pyrethroids), OCs demonstrated the lowest added toxicity detected in this study.

As can be observed by reviewing the barplots of average concentrations of OCs detected in each subregion (Figure 1), wide variability in type and concentration of OCs exists across subregions. The Lower Pajaro subregion had the highest average concentrations for many of the legacy OC compounds while Santa Ynez, Santa Barbara area creeks, San Luis Obispo creeks and the middle mainstem of the Salinas River all had much lower average concentrations of legacy OCs. The median concentrations of the current use OCs, dicofol and DCPA, were highest in the Lower Salinas area tributaries and Reclamation Canal watershed (Dicofol 13.3 ng/g, DCPA 15.6 ng/g).

Concentrations of OC pesticides detected are shown in Table 4. Added TUs of OC compounds for *H. azteca* are shown in Table 6. Although TUs do not always have an additive effect, the added TU values can inform an initial rough assessment. Individual OC toxic unit calculations for each site for *H. azteca* (where an LC_{50} could be found) are shown in Table 7. A barplot of average concentrations of individual OCs found in monitored sediments by subregion are shown in Figure 1. Maps depicting monitoring sites and showing added TUs of OCs compared with other pesticide classes are shown in Figures 4 through 9. When considering average values, note that the sites monitored for the CMP were selected to reflect agricultural inputs and existing known impairments, and results are not intended to be representative of overall water quality in the Central Coast region nor in any subregions.

For specific areas of interest identified below, pesticides with multiple forms were added and reported together. Therefore, DDD includes both 2,4'-DDD and 4,4'-DDD. Similarly, DDE and DDT include both forms. Cis and trans forms of both chlordane and nonachlor were added and reported together. For specific concentrations at sites separated by forms, refer to Table 4.

3.1.1 Pajaro River watershed organochlorine results

The following OC's were detected at the 10 Pajaro River watershed monitoring sites during this study: DDD (8 sites), DDE (10 sites), DDT (5 sites), chlordane (3 sites), nonachlor (2 sites), dieldrin (1 site), toxaphene (4 sites), and dicofol (5 sites). Endrin, perthane and DCPA were not detected at any Pajaro watershed site, nor were the other OC pesticides listed in Section 3.1 as not detected at any sites during this study. Dicofol was the only current use OC detected in the Pajaro watershed, found at the following 5 sites: 305COR, 305PJP, 305WSA, 305LCS and 305SJA. The only site with added TUs greater than 0.01 associated with OC pesticides was Watsonville Slough (305WSA) with 0.09 TUs. A map depicting monitoring sites and showing added TUs of OCs for *H. azteca* compared with other pesticide classes is displayed in Figure 4.

3.1.2 Mainstem Salinas River organochlorine results

Four mainstem Salinas River sites were sampled. At the Chualar bridge on River Rd. (309SAC), the legacy OC, DDD, the breakdown product, DDE, and the current use DCPA were detected. At Salinas River at the Spreckels gage (site 309SSP), legacy DDD, DDT and DDE were detected and DCPA was detected. No legacy OC pesticides except the by-product DDE were detected at the other 2 sites sampled on the mainstem Salinas River, Greenfield (309GRN) and Gonzales (309SAG), and no current use OCs were detected at these two sites either. Organochlorine added TUs for all sites in this subregion were all 0.00. A map depicting monitoring sites and showing added TUs of OCs for *H. azteca*. compared with other pesticide classes is displayed in Figure 5.

3.1.3 Lower Salinas Tributary and Reclamation Canal organochlorine results

The following OCs were detected at the 12 Lower Salinas tributaries and Reclamation Canal monitoring sites during this study: DDD (11 sites), DDE (12 sites), DDT (9 sites), chlordane (9 sites), nonachlor (8 sites), dieldrin (9 sites), perthane (1 site), toxaphene (11 sites), DCPA (7 sites), and dicofol (6 sites). Endrin was not detected at any sites in this area, nor were the other OC pesticides listed in Section 3.1 as not detected at any sites during this study. The current use OC pesticides, DCPA and dicofol were both detected at the three tributary sites east of Salinas and at three additional sites west of Salinas: 309ALG, 309BLA, 309CRR, 309JON, 309QUI, and 309TEH. Dicofol (but not DCPA) was detected at 309ASB, 309ESP, and 309OLD. DCPA (but not dicofol) was detected at 309MER. Organochlorine added TUs for all sites in this subregion ranged from 0.00 to 0.06 (Table 6). A map depicting monitoring sites and showing added TUs of OCs compared with other pesticide classes for *H. azteca* is displayed in Figure 5.

3.1.4 Santa Maria organochlorine results

The following OCs were detected at the 9 Santa Maria sites monitored during this study: DDD (9 sites), DDE (9 sites), DDT (8 sites), chlordane (2 sites), nonachlor (2 sites), dieldrin (4 sites), toxaphene (9 sites), and dicofol (6 sites). Endrin, perthane and DCPA were not detected at any sites in this area, nor were the other OC pesticides listed in Section 3.1 as not detected at any sites during this study. The Santa Maria River at Highway 1 did not have flowing water and could not be monitored (312SMI). The current use OC pesticide, dicofol was detected at 6 Santa Maria sites (312BCJ, 312GVS, 312MSD, 312OFC, 312ORC, 312ORI). Organochlorine added TUs for all sites in this subregion ranged from 0.0 to 0.05 (Table 6). A map depicting monitoring sites and showing added TUs of OCs for *H. azteca* compared with other pesticide classes is displayed in Figure 6.

3.1.5 San Luis Obispo, Santa Ynez, and Santa Barbara Creeks area organochlorine results

The following OCs were detected among the 11 SMU monitoring sites outside of the Santa Maria area during this study: DDD (2 sites), DDE (5 sites), chlordane (1 site), nonachlor (1 site), toxaphene (1 sites),

and DCPA (1 site). DDT, dieldrin, endrin, perthane and dicofol were not detected at any of these sites, nor were the other OC pesticides listed in Section 3.1 as not detected at any sites. The only site with detection of a current use OC was in San Luis Obispo at Warden Creek (310WRP) where DCPA was detected. Two sites did not have flowing water and could not be monitored (310LBC & 310SLD). Organochlorine added TUs for all sites in this subregion were less than 0.01. Maps depicting monitoring sites and showing added TUs of OCs compared with other pesticide classes for *H. azteca* are displayed in Figures 7 through 9.

3.2 Pyrethroid Pesticide Results

Pyrethroids are a class of pesticides with biological origins from plants that evolved to develop natural chemicals to resist insects (Kamrin 1997). Pyrethrum is the extracted botanical product, however it tends to break down quickly in the environment, so longer lasting compounds have been synthesized for use in agricultural and urban pesticides. Modern synthetic pyrethroids are more potent, have a longer half life and are more persistent in the environment than pyrethrum (Kamrin 1997). Through interfering with the balance of sodium junctions in nerve endings, they exert a toxic effect. Most pyrethroid compounds display a strong tendency to adsorb to soil particles, especially particles with high organic carbon content (Montgomery 1977, Kamrin 1997), thereby making them more likely to be found in bed sediments than dissolved in the water column. However, water samples containing suspended sediments can also contain pyrethroids sorbed to particles. Twelve pyrethroids were analyzed: allethrin, bifenthrin, cyfluthrin, cypermethrin, danitol (fenpropathrin), deltamethrin, esfenvalerate, fenvalerate, fluvalinate, lambda-cyhalothrin, permethrin and prallethrin. Of the 12 pyrethroids analyzed, 10 were detected at one or more sites in the study area. Neither deltamethrin nor prallethrin were detected at any sites.

At least 1 pyrethroid was detected in sediments at 31 of the 46 sites sampled and 9 individual pyrethroids were detected at 2 sites. Allethrin was only detected at 1 site (312BCJ) at a low concentration (0.6 ng/g) below the reporting limit (RL). Pyrethroids with detections at more than 5% of the sites sampled included bifenthrin (25 sites, 54%) , lambda-cyhalothrin (23 sites, 50%), cypermethrin (21 sites, 46%), danitol (18 sites, 39%), esfenvalerate (18 sites, 39%), cyfluthrin (17 sites, 37%), permethrin (17 sites, 37%), fenvalerate (16 sites, 35%), and fluvalinate (4 sites, 9%).

Individual pyrethroids (where an LC_{50} could be identified in the literature) detected in sediments with concentrations greater than 0.5 TUs for *H. azteca* were bifenthrin (14 sites), cyfluthrin (3 sites), cypermethrin (7 sites), danitol (3 sites), esfenvalerate (2 sites), fenvalerate (1 site), lambda-cyhalothrin (12 sites), and permethrin (4 sites). Toxic units could not be computed for allethrin and fluvalinate because an LC_{50} value for *H. azteca* was not found during the literature review. Toxic units for individual pyrethroids ranged from 0.0 to 32.5 (bifenthrin at 312BCJ). Compared with the other two pesticide classes (OPs and OCs), added pyrethroid TUs were consistently higher in sediments (Figures 4-9).

Subregional averages for pyrethroids detected in this study are shown in Figure 2. Average pyrethroid concentrations were considerably higher in the Santa Maria area than in other subregions, with relatively high average amounts of permethrin, danitol and bifenthrin found in this area. These averages may be somewhat elevated by the high concentrations above 195 ng/g of each of these three pesticides found at 1 or 2 sites. The area with the second highest averages for pyrethroid concentrations in sediments was lower Salinas tributaries and Reclamation Canal with relatively high concentrations of permethrin, lambda-cyhalothrin, and bifenthrin. When considering average values, note that the sites monitored for the CMP were selected to reflect agricultural inputs and existing known impairments, and results are not intended to be representative of overall water quality in the Central Coast region nor in any subregions.

Concentrations of pyrethroids detected are shown in Table 5. Added TUs of pyrethoid compounds for *H. azteca* are shown in Table 6. Toxic unit calculations for *H. azteca* (where an LC_{50} could be found) are

shown in Table 7. Barplots of average concentrations of individual pyrethroids found in sampled sediments by subregion are shown in Figure 2. Maps depicting monitoring sites and showing added TUs of pyrethroids compared with other pesticide classes are shown in Figures 4 through 9. A barplot for each detected pyrethroids showing the number of sites with greater than 0.5 TUs by subregion is shown in Figure 11.

3.2.1 Pajaro River watershed pyrethroid results

The following pyrethroids were detected at the 10 Pajaro River watershed monitoring sites during this study: bifenthrin (5 sites), cyfluthrin (2 sites), cypermethrin (3 sites), danitol (2 sites), esfenvalerate (1 site), fenvalerate (1 site), lambda-cyhalothrin (4 sites), and permethrin (1 site). The following pyrethroids were not detected at any sites in the Pajaro watershed: allethrin, deltamethrin, fluvalinate, and prallethrin. Sites with no detections of any pyrethroids in the Upper Pajaro watershed were 305CAN, 305CHI, 305FRA, and 305TSR (Table 5; Fig. 4). Bifenthrin (1.9 ng/g) and cyfluthrin (0.6 ng/g) were detected in sediments at Llagas Creek (305LCS). Cypermethrin (4.6 ng/g), lambda-cyhalothrin (20.6 ng/g) and permethrin (77.7 ng/g) were detected in sediments from San Juan Creek (305SJA). In the Lower Pajaro watershed, pyrethroids were detected in sediments at all 4 sites (refer to Table 5 for specific concentrations).

The highest toxic potential of an individual pyrethroid in the Pajaro watershed was lambda-cyhalothrin (2.47 TUs) in San Juan Creek (305SJA). At this same location (305SJA), cypermethrin toxic potential was measured at 0.65 TUs and permethrin at 0.39 TUs. The highest total added pyrethroid TUs was in San Juan Creek (305SJA; 3.52 TUs) and other sites in this subregion had added pyrethroid TUs ranging from 0.0 to 1.35 (Table 6). A map depicting monitoring sites and showing added TUs of pyrethroids for *H. azteca* compared with other pesticide classes is displayed in Figure 4.

3.2.2 Mainstem Salinas River pyrethroid results

Four mainstem Salinas River sites were sampled. No pyrethroids were detected for the Salinas River at Chualar bridge on River Rd. (309SAC) , at Greenfield (309GRN) nor at Gonzalez (309SAG). At the Spreckel's gage (309SSP), both lambda-cyhalothrin (concentration below the RL) and bifenthrin (2.7 ng/g) were detected. Added pyrethroids TUs were 0.0 at all sites in this subregion except 309SSP (0.56 TUs). A map depicting monitoring sites and showing added TUs of pyrethroids for *H. azteca* compared with other pesticide classes is displayed in Figure 5.

3.2.3 Lower Salinas Tributary and Reclamation Canal pyrethroid results

Two or more pyrethroids were detected at 11 out of the 12 sites sampled from lower Salinas tributaries and the Reclamation Canal watershed. Pyrethroids were not detected in Chualar Creek (309CRR). The following pyrethroids were detected in sediments at the other sites in this subregion: bifenthrin (10 sites), cyfluthrin (6 sites), cypermethrin (9 sites), danitol (8 sites), esfenvalerate (9 sites), fenvalerate (8 sites), fluvalinate (3 sites), lambda-cyhalothrin (9 sites), and permethrin (8 sites). The pyrethroids not detected at any sites were allethrin, deltamethrin, and prallethrin. The highest concentration of an individual pyrethroid was permethrin [68.1 ng/g in the Salinas Reclamation Canal (309JON) and 43.9 ng/g in Merrit Ditch (309MER); Table 5]. Concentrations of other individual pyrethroids detected are shown in Table 5. The highest TUs in this subregion were associated with bifenthrin (7.5 TUs in 309JON) and lambda-cyhalothrin (6.7 TUs in 309QUI; Table 7). A map depicting monitoring sites and showing added TUs of pyrethroids compared with other pesticide classes for *H. azteca* is displayed in Figure 5.

3.2.4 Santa Maria pyrethroid results

One or more pyrethroids were detected in bed sediment at all 9 sites sampled from the Santa Maria watershed. The Santa Maria River at Highway 1 did not have flowing water and could not be monitored (312SMI). The only pyrethroid detected in the Santa Maria River Estuary (312SMA) was cyfluthrin (0.9 ng/g) at a concentration below the RL. The following pyrethroids were detected in sediments in the Santa Maria watershed monitored during this study: allethrin (1 site), bifenthrin (8 sites), cyfluthrin (6 sites), cypermethrin (7 sites), danitol (8 sites), esfenvalerate (8 sites), fenvalerate (7 sites), lambda-cyhalothrin (8 sites), and permethrin (8 sites). Allethrin (0.6 ng/g) was detected in Bradley Channel (312BCJ) at a concentration below the RL. The pyrethroids not detected at any sites in the Santa Maria watershed were fluvalinate, deltamethrin and prallethrin. The individual pyrethroids detected at the highest concentrations in this subregion were permethrin [286.4 ng/g in Bradley Channel (312BCJ) & 266.7 ng/g in the Main Street ditch (312MSD)] , bifenthrin [216.4 ng/g at Bradley Channel (312BCJ)] and danitol [195.4 ng/g in Little Oso Flaco Creek (312OFN); Table 5]. Pyrethroids at concentrations with the highest toxic potential were bifenthrin [32.5 TUs in 312BCJ, 5.4 TUs in Oso Flaco Creek (312OFC) & 3.5 TUs in 312OFN] and lambda-cyhalothrin [3.1 TUs in 312BCJ and 2.5 TUs in Green Valley (312GVS); Table 7]. A map depicting monitoring sites and showing added TUs of pyrethroids for *H. azteca* compared with other pesticide classes is displayed in Figure 6.

3.2.5 San Luis Obispo, Santa Ynez, and Santa Barbara Creeks pyrethroid results

Pyrethroids were not detected at any of the 3 Santa Ynez sites monitored (314SYF, 314SYL, 314SYN). No pyrethroids were detected in the 4 Santa Barbara coastal creek sites, with the exception of fluvalinate (6.0 ng/g) in Franklin Creek (315FMV). In the San Luis Obispo (SLO) area, two sites (310LBC and 310SLD) did not have flowing water and could not be sampled. No pyrethoids were detected in Chorro Creek (310CCC). Individual pyrethroids with the highest concentrations in SLO were cyfluthrin [15.9 ng/g in Prefumo Creek (310PRE)] and cypermethrin (4.8 ng/g at 310PRE; Table 5). Pyrethroids with the highest toxic potential detected in SLO were cyfluthrin (0.14 TUs at 310PRE) and cypermethrin [0.14 TUs in Arroyo Grande Creek (310USG)]. Although cypermethrin was detected at a higher concentration at 310PRE than at 310USG, the influence of TOC resulted in a calculation of higher TUs at 310USG. Maps depicting monitoring sites and showing added TUs of pyrethroids compared with other pesticide classes for *H. azteca* are displayed in Figures 7 through 9.

3.3 Organophosphate Pesticide (Chlorpyrifos) Results

The only OP pesticide analyzed in benthic sediments in this study was chlorpyrifos. Chlorpyrifos was placed in re-evaluation by the California Department of Pesticide Regulation (CA DPR) in April 2004 due to detection in numerous California water-bodies at levels toxic to aquatic life (CA DPR 2004). The CA DPR identified agriculture as the principle source of chlorpyrifos. Chlorpyrifos was detected at 21 of the 46 sites sampled. Toxic units for chlorpyrifos were more than 0.50 TUs at 14 sites and more than 1.0 TUs at 6 of the 46 sites sampled. Toxic units in sediment normalized by organic carbon content for chlorpyrifos ranged from 0.33 to 2.78 at sites where chlorpyrifos was detected. To derive TUs, the LC_{50} value 1.77 ug/g o.c. was used (Brown et al. 1997, Amweg and Weston 2007).

Subregional averages for chlorpyrifos found in sampled sediments in this study are displayed in the barplot in Figure 3. The Santa Maria area had the highest average concentrations, followed by Lower Salinas area tributaries & Reclamation Canal and the mainstem Salinas River. This pattern was driven by the fact that chlorpyrifos was not detected outside of the Salinas and Santa Maria watersheds.

Concentrations of chlorpyrifos detected in sediments from each site are shown in Table 5. Toxic unit calculations for *H. azteca* are shown in Table 7. Maps depicting monitoring sites and showing added TUs of chlorpyrifos compared with other pesticide classes are shown in Figures 4 through 9. When considering average values, note that the sites monitored for the CMP were selected to reflect agricultural inputs and existing known impairments, and results are not intended to be representative of overall water quality in the Central Coast region nor in any subregions.

3.3.1 Pajaro River watershed organophosphate results

Chlorpyrifos was not detected in sediments at any of the 10 Pajaro River watershed sites monitored. A map depicting monitoring sites and showing TUs (0 at all sites in this subregion) of chlorpyrifos for *H azteca* compared with other pesticide classes is displayed in Figure 4.

3.3.2 Mainstem Salinas River organophosphate results

Four mainstem Salinas River sites were sampled. Chlorpyrifos was not detected in sediments from the Salinas River at Greenfield (309GRN) nor at Gonzalez (309SAG). It was detected in sediments from the Chualar bridge (309SAC) at a concentration of 12.8 ng/g, equivalent to 0.26 TUs. It was the only pesticide contributing to sediment TUs detected at this site. Chlorpyrifos was also detected the Salinas River at Spreckels (309SSP), at a concentration of 7.9 ng/g, equivalent to 0.38 TUs (Table 5). Toxic units were higher at 309SSP than at 309SAC despite lower concentrations due to the relatively lower TOC at 309SSP. A map depicting monitoring sites and showing TUs of chlorpyrifos compared with other pesticide classes for *H. azteca* is displayed in Figure 5.

3.3.3 Lower Salinas Tributary and Reclamation Canal organophosphate results

Chlorpyrifos was detected in sediment from 10 of the 12 sites sampled in the Lower Salinas tributaries and Reclamation Canal watershed at concentrations ranging from 11 ng/g in Blanco Drain (309BLA) to 37.6 ng/g in the Salinas Reclamation Canal at La Guardia (309ALG; Table 5). No chlorpyrifos was detected at Moro Coho Slough at Highway 1 (306MOR) nor in Natividad Creek (309NAD). The highest toxic potential of chlorpyrifos in this subregion was 2.19 TUs (309QUI; Table 7). A map depicting monitoring sites and showing added TUs of chlorpyrifos compared with other pesticide classes for *H. azteca* is displayed in Figure 5.

3.3.4 Santa Maria organophosphate results

Chlorpyrifos was detected at all 9 Santa Maria sites sampled. The Santa Maria River at Highway 1 did not have flowing water and could not be monitored (312SMI). Chlorpyrifos concentration ranged from 9.6 ng/g in Oso Flaco Creek (312OFC) to 63.0 ng/g in Bradley Channel (312BCJ; Table 5). The toxic potential of chlorpyrifos in this watershed ranged from 0.55 TUs in the Santa Maria Estuary (312SMA) to 2.78 TUs in Bradley Channel (312BCJ; Table 7). Because TUs are calculated taking into account both pesticide concentration and TOC, in some cases the lowest number of TUs is not found at the site with the lowest concentration. A map depicting monitoring sites and showing added TUs of chlorpyrifos for *H. azteca* compared with other pesticide classes is displayed in Figure 6.

3.3.5 San Luis Obispo, Santa Ynez, and Santa Barbara Creeks area organophosphate results

Chlorpyrifos was not detected in sediments at any of the 11 sites sampled in these three subregions (Table 5). Two sites (310LBC and 310SLD) did not have flowing water and could not be sampled. Maps depicting monitoring sites and showing added TUs of chlorpyrifos compared with other pesticide classes for *H. azteca* is displayed in Figures 7 through 9.

3.4 Toxicity: Survival and Growth of *Hyalella azteca*

Sediments for the freshwater sediment toxicity tests with *H. azteca* for effects on survival and growth were collected concurrently with each sample for pesticide analysis (i.e. 49 samples from 46 sites during a single monitoring event in May 2010). Based on the results of statistical analysis using the CETIS® statistical software package, survival rates for test organisms were significantly lower than the control in 28 of the 49 samples, or 57% of samples. As 3 samples were duplicates taken at the same site, significantly reduced survival was present at 27 of the 46 sites, or 59% of sites sampled. Survival rates of the test organism, when survival was significantly reduced, ranged from 0% to 91 % of control organism survival. Site-specific invertebrate survival rates are provided in Table 6 and displayed by subregion in Figures 10a through 10d.

Statistically significant effects on growth rates for test organisms could only be assessed when there was not a significant survival effect. Of the 19 samples which were tested for growth, growth rates were significantly lower than the control in 1 sample. Site-specific results for invertebrate growth rates are provided in Table 6.

3.4.1 Pajaro River watershed toxicity results

Survival-based toxicity in sediment was observed at 3 of the 10 sites monitored in the Pajaro River watershed during the May 2010 monitoring event. These three sites were Salsipuedes Creek (305COR , Watsonville Slough (305WSA), and San Juan Creek (305SJA). At 305COR added pyrethroids were less than 0.5 TUs, therefore the observed toxicity may be better explained by the presence of other toxicants as described in the Discusson section (4.1) of this report. It is also possible that the observed pyrethroids *do* explain some or all of the toxicity, as they summed to nearly 0.4 TUs, and sediments can show substantial spatial heterogeneity. At 305SJA two pyrethroid pesticides (cypermethrin and lambda-cyhalothrin) were measured at > 0.5 TUs. At 305WSA, bifenthrin was measured at > 0.5 TUs. At these two sites, though unmeasured toxicants may also have been present, the observed toxicity may be explained by the measured pesticides. Percent survival rates were 75%, 65% and 25% of the control, respectively. No survival-based toxicity or growth related effects to invertebrates were observed in the mainstem Pajaro River [at Chittenden (305CHI) or at Main St (305PJP)], in Struve Slough (305STL), nor in Llagas Creek (305LCS). Although survival-based toxicity was not observed in Millers Canal (305FRA), growth related effects were significant.

3.4.2 Mainstem Salinas River toxicity results

Survival-based toxicity to *H. azteca* was observed at 2 sites on the mainstem Salinas River, at Chualar bridge at River Rd (309SAC) and the Spreckel's Gage (309SSP). Added TUs at 309SAC were less than 0.5 TUs, so survival based toxicity at this site may be related in part to other toxicants as described in Section 4.1 of this report. Although no individual pesticide was found at a concentration > 0.5TUs at 309SSP, added bifenthrin and lambda-cyhalothrin were just over 0.5 TUs, so the observed toxicity may be explained at least in part by the combination of measured pesticides. Percent survival rates were 91% and 89 % respectively. Toxicity was not observed at either 309GRN nor at 309SAG, and neither site had detections of single or additive pesticides at >0.5 TUs. No significant reduction in growth rates were observed at any the 4 sites monitored either.

3.4.3 Lower Salinas Tributary and Reclamation Canal watershed toxicity results

Survival-based toxicity in sediments was observed at 10 of the 12 sites monitored in lower Salinas tributaries and Reclamation Canal watershed. The 2 sites where no significant toxicity was observed were Blanco Drain (309BLA) and Alisal Slough (309ASB). No individual pesticides were detected at either 309BLA or 309ASB above the 0.5 TUs benchmark, however added TUs of 4 different pyrethroids were greater than 0.5 TUs in both cases. These two sites did not show statistically significant mortality, however survival in the 309BLA sample was 10% lower than the control. Although toxicity was observed at 306MOR and 309CRR, added TUs at both sites were less than 0.5 TUs, perhaps indicating the presence of other toxicants as described in Section 4.1 of this report. At all other sites demonstrating significant mortality-related toxic effects (309ALG, 309ESP, 309JON, 309MER, 309NAD, 309OLD, 309QUI, and 309TEH), at least one individual pesticide was present at concentrations >0.5 TUs, so the observed toxicity may be explained at least in part by the measured pesticides. Pesticides found at concentrations above this benchmark included bifenthrin at 7 sites, cyfluthrin at 1 site, cypermethrin at 4 sites, esfenvalerate at 1 site, fenvalerate at 1 site, lambda-cyhalothrin at 6 sites and permethrin at 1 site. There was 0% survival in the Salinas Reclamation Canal at La Guardia (309ALG). Survival at other sites in this area ranged from 5% in Natividad Creek (309NAD) to 99% in Alisal Slough (309ASB).

3.4.4 Santa Maria watershed toxicity results

Survival-based toxicity in sediments was observed at all 9 sites sampled during the May 2010 monitoring event in the Santa Maria watershed. At all sites except at the Santa Maria River at the estuary (312SMA), pyrethroids were detected in concentrations that summed to > 0.5 TUs. Individual pyrethroids detected at >0.5 TUs were bifenthrin at 6 sites, cyfluthrin at 2 sites, cypermethrin at 2 sites, esfenvalerate at 1 site, lambda-cyhalothrin at 5 sites, and permethrin at 3 sites. Chlorpyrifos concentrations exceeded 0.5 TUs at all Santa Maria sites sampled. Based on the concentrations detected, observed toxicity to invertebrates may be explained at least in part by the measured pesticides at all sites sampled in Santa Maria. Survival was 0% at the following 5 sites: Main Street Canal (312MSD), Oso Flaco Creek (312OFC), Little Oso Flaco Creek (312OFN), Orcutt Solomon Creek upstream of the Santa Maria River (312ORC), and the Bradley Channel at Jones St. (312BCJ). Survival at other sites in this area ranged from 5% in Green Valley (312GVS) to 65% in Orcutt Solomon Creek at Highway 1 (312ORI).

3.4.5 San Luis Obispo, Santa Ynez, and South Coast area toxicity results

Survival-based toxicity in sediments was observed at 3 sites in these other SMU areas - in the San Luis Obispo area at Warden Creek (310WRP) and in Santa Barbara coastal creeks at both Arroyo Paredon (315APF) and Franklin Creek (315FMV). Survival based toxicity was not explained by the pesticides detected at any of these sampling sites, as all individual pesticides and added pesticide concentrations were far below the 0.5 TUs benchmark, perhaps indicating the presence of other toxicants as described in Section 4.1 of this report. For example, heavy metals, several other pesticide classes, and porewater ammonia were not measured in this study. Survival rates compared with control results at 310WRP, 315APF and 315FMV were 63%, 59% and 61%, respectively.

4 DISCUSSION

This study represents the first sediment-related pesticide monitoring undertaken by the CMP and is also one of the more spatially extensive studies of sediment toxicity and pesticide concentrations to date in the Central Coast region of California, with a total of 44 pesticides analyzed at 46 sites in six different counties. Important context for interpreting the results of this study is that CMP sites were selected in

2004 based on known, existing water quality impairments. Though not all impairments are toxicity-related, some degree of degradation is generally expected at every site; therefore this group of sites does not represent the general condition of waterbodies in the Central Coast region. Furthermore, the sites monitored were chosen to represent impacts from surrounding agricultural lands, so impairments are likely of agricultural origin in many cases. That said, upstream urban land uses also contribute to runoff and sediment chemistry at several sites. In addition to urban land uses, some sites are maintained by agencies to provide drainage for major highways, which may introduce impacts from non-agricultural herbicides.

4.1 Relationship Between Pesticides in Sediment and Toxicity

Toxic unit (TU) calculations normalized for sediment organic carbon content for each pesticide were calculated when an LC_{50} could be identified in the literature. Toxic unit calculations for individual pesticides at each site are shown in Table 7. Toxic units were added within pesticide classes and across classes as shown in Table 6. Weston et al. (2004) suggested that a threshold of 0.5 TUs indicates an individual compound is likely to be responsible for making a substantial contribution to mortality observed in a laboratory toxicity test. Although the authors explain that the specific threshold of 0.5 TUs was not initially deliberately chosen, their data indicated that pesticides present at or above this level of TUs were strongly linked to toxicity to *H. azteca* in their research in California's Central Valley (Weston et al. 2004). In other words, there is evidence to support 0.5 TUs as a biologically meaningful threshold. This 0.5 TU threshold appears applicable on the Central Coast as well, as all CMP sites in this study where an individual pesticide was present at a concentration greater than this threshold (>0.5 TUs) showed toxicity to *H. azteca* in concurrent toxicity tests. As most sites contained mixtures of pesticides however, it is not possible in these cases to attribute toxicity to any individual pesticide, even at concentrations above the 0.5 TU threshold. Further study would be required to answer this question, including investigation of toxicants not analyzed in this study.

Comparison of survival rates to added TUs across all pesticide classes shows a fairly intuitive relationship, with generally lower survival at higher TUs (Fig. 12). In all cases (i.e. 19 sites) where at least one individual pesticide was detected in concentrations greater than 0.5 TUs, significant mortality was observed in concurrent toxicity tests. Statistically significant mortality observed at sites with less than 0.5 TUs could be due to interactive pesticide toxicity (i.e. synergistic effects beyond additive effects) or to other factors, which may include pesticides not analyzed or other toxicants in sediment samples. Because of the non-homogenous nature of sediments, it is also possible that two sediment samples taken from the same location did not share identical chemistries, such that different pesticide concentrations could be present in sediment aliquots analyzed for toxicity versus those analyzed for pesticide concentrations. Toxic unit calculations for both legacy and current use OC compounds indicated these were present only at concentrations less than 0.1 TU. The only OP analyzed in sediment, chlorpyrifos, was present at concentrations with TUs >0.5 at 14 sites and likely contributed to toxicity at these sites. Pyrethroids were the class of pesticides most associated with sediment toxicity with pyrethroid TUs >0.5 at 19 sites. Individual pyrethroids detected at concentrations over the 0.5 TU threshold included bifenthrin (14 sites), cyfluthrin (3 sites), cypermethrin (7 sites), danitol (3 sites), esfenvalerate (2 sites), fenvalerate (1 site), lambda cyhalothrin (11 sites), and permethrin (4 sites). Both chlorpyrifos and one or more pyrethroids may have contributed to toxicity at the same site.

It is important to note that pyrethroids and chlorpyrifos were detected individually or in combination at amounts >0.5 TUs in many of the sediments found to be toxic to *H. azteca*. Both added pyrethroids and chlorpyrifos were present at concentrations greater than the 0.5 TU benchmark at 48% of sites (i.e. 13 out of 27). At one site only chlorpyrifos was greater than 0.5 TUs, and at 5 sites only added pyrethroids were greater than 0.5 TUs. Although not all observed toxicity is explained by pesticides in sediments (i.e. a few sites had low survival despite low measured pesticide concentrations), there is an apparent

relationship (qualitative) between TUs and percent survival. All but two samples with total TUs (summed from all pesticide classes) >5.0 had significantly reduced survival rates.

Unionized ammonia is also toxic to aquatic invertebrates and comes from both natural and anthropogenic sources (e.g. fertilizer). The search for LC_{50} for unionized ammonia for *H. azteca* in sediments revealed one study concluding that this invertebrate avoided interstitial contaminated water by escaping to overlying water, thus obfuscating the determination of an LC_{50} (Whiteman et al. 1996).

4.1.1 Organochlorines and potential impact on sediment toxicity

Many of the organochlorine (OC) pesticides analyzed and detected are no longer in use or are severely restricted by the US EPA. The detection of DDT at 66% of sites in the lower Salinas area during this study generally corroborates with a 2004 Central Coast Watershed Studies finding that some form of DDT was detected at 78% of sites (Kozlowski et al. 2004). Of the current use OC pesticides, only DCPA and dicofol were detected. DCPA is an herbicide used for the control of pre-emergent weeds (USEPA 1998). Overall the USEPA (1998) finds DCPA to have very low toxicity to mammals, to be slightly toxic to fish and aquatic invertebrates, and highly toxic to non-target estuarine and marine organisms. An EPA report concerning the federally threatened California Red-legged Frogs (*Rana aurora draytonii*) reported a preliminary finding that DCPA use "may affect" determination of Federal Insecticide, Fungicide, Rodenticide Act (FIFRA) regulatory action and determined DCPA usage was "likely to adversely affect" California Red-legged Frogs (USEPA 2009a). DCPA was detected at 10 of the 46 sample locations (22% of sites), with the highest concentrations of 217.3 ng/g (ppb – parts per billion) and 289 ng/g at Chualar Creek (309CRR) and Quail Creek (309QUI) respectively. Both of these sites are directly adjacent to Highway 101and may be subject to weed control and other maintenance activities by non-agricultural entities. Because an LC_{50} could not be found for DCPA, no TUs could be derived for the purposes of relative toxicity evaluation or risk analysis for this material. Dicofol is a broad-spectrum acaricide, insecticide and miticide used on fruits, vegetables and ornamental plants that is very highly to highly toxic to freshwater fish and highly toxic to aquatic invertebrates (USEPA 2009b). The USEPA risk assessment of California Red-legged Frog declared dicofol "may affect" determination of FIFRA regulatory action and recommended initiating a formal consultation with the US Fish and Wildlife Service under the Endangered Species Act (USEPA 2009b). Dicofol was detected at 20 of the 46 sites monitored (46% of sites) in concentrations up to 55 ng/g found in the Watsonville Slough (305WSA). Although as yet unpublished, the LC_{50} value of 250 ng/g (in review, Weston 2010) for dicofol indicated estimated TUs of 0.01 at this location.

4.1.2 Pyrethroids and potential impact on sediment toxicity

Several pyrethroids were simultaneously placed into reevaluation on August 31, 2006 by the California Department of Pesticide Regulation (CA DPR) due to their frequent detection at levels toxic to *H. azteca* in bed sediments in watersheds dominated by agricultural and urban landscapes (CA DPR 2006). Frequent detection and presence of pyrethroids in waterbodies at concentrations known to compromise the health and survival of *H. azteca* were confirmed by this study. The detection rate for pyrethroid pesticides in the May 2010 CMP monitoring event was 31 out of 46 sites (70%), with more detections in the Santa Maria (100%), Salinas (80%), and San Luis Obispo (75%) areas as compared with the Pajaro (60%), Santa Barbara (25%), and Santa Ynez (0%) areas. By comparison, a CA DPR study in 2004 found an overall pyrethroid detection rate of 30% in four California agricultural regions (Salinas River, Northern San Joaquin Valley, Sacramento Valley/Feather River, and Imperial Valley) and a detection rate of 60% in Salinas (Starner and Kelley 2004). Detections of pyrethroids at concentrations greater than 0.5 TUs occurred at 41% of sites monitored. In the CMP study, detections at concentrations greater than the 0.5 TUs benchmark occurred for the following active ingredients: bifenthrin (14 sites), cyfluthrin (3

sites), cypermethrin (7 sites), danitol (3 sites), esfenvalerate (2 sites), fenvalerate (1 site), lambda-cyhalothrin (12 sites), permethrin (4 sites; Fig. 11 & Table 7).

Because pyrethroids were present in concentrations >0.5 TUs at many sites in this study, it is also worth noting the influence of water temperature on pyrethroid-related toxicity. As water temperature decreases pyrethroids become more toxic (Weston et al. 2009). The U.S. EPA testing protocol standard for toxicity testing is 23˚C, however pyrethroids are twice as toxic at a temperature of 18˚C and three times as toxic at 13˚C (Weston et al. 2009). The sites monitored during this study ranged in temperature from 16˚C to 25˚C during May2010 monitoring and were generally cooler than the EPA standard of 23˚C, so actual toxicity of pyrethroids to organisms resident in these waterbodies may be somewhat under-estimated by these laboratory toxicity tests.

4.1.3 Organophosphates and potential impact on sediment toxicity

Prior CMP Follow-up monitoring for OPs in water and also in this study (sediments) showed that chlorpyrifos is present in both the water column and sediments of Salinas and Santa Maria waterbodies. Chlorpyrifos was not detected in sediments during the May 2010 monitoring event in the Pajaro, San Luis Obispo, Santa Barbara or Santa Ynez areas; however it was detected in all 9 Santa Maria sites (100%) and in 12 out of 16 sites (75%) in the Salinas/Castroville areas. During the 2006 & 2007 Follow-up monitoring of water column OPs, chlorpyrifos was detected at least once at 80% of Santa Maria sites and 62% of Salinas sites monitored (CCWQP 2009). During 2009 Follow-up monitoring outside of the Salinas and Santa Maria areas, chlorpyrifos in the water column was detected only in February (but not in January, August or September) at Arroyo Grande Creek in San Luis Obispo (310USG) and at Franklin Creek in Carpinteria (315FMV; CCWQP 2010b).

4.1.4 Pesticide mixtures and potential impact on sediment toxicity

Mixtures of pesticides occur at many of the sites monitored with more than 5 compounds detected at each of 26 sites and 24 co-occurring in the Tembladero Slough (309TEH). Mixtures rather than individual toxicants are often implicated in laboratory toxicity findings (Anderson et al. 2007). However, determining the toxicity of combinations of pesticides is difficult as the number of combinations is vast and toxicity may be independent or interactive, with interactive effects including effects that are additive, antagonistic, or synergistic in their effect on aquatic organisms. As an example, piperonyl butoxide (PBO) is added to some pyrethroids pesticide products as a synergist to increase their potency (Amweg and Weston 2007). While its effect is synergistic in combination with pyrethroids, creating a stronger-than-added toxic effect, it is antagonistic to chlorpyrifos and weakens its effect (Amweg and Weston 2007). Despite synergistic effects, adding TUs to estimate overall site toxicity is a common practice, especially among pesticides of the same class sharing a common mechanism (Bailey et al. 1997, Junghans et al. 2003, Weston et al. 2004, Ding 2009). For example, both chlorpyrifos and diazinon inhibit the activity of acetylcholinesterase and their combined effect is additive for aquatic invertebrates (Bailey et al. 1997, Siepmann and Finlayson 2000). Laetz et al. (2009) observed both added and synergistic effects of carbamate and organophosphate (OP) pesticides on juvenile Pacific salmon. Whereas added effects were found at lower concentrations, OP mixtures demonstrated synergistic effects (greater than additive) on juvenile salmon as pesticide concentrations increased. In mixtures where the mechanism is dissimilar, Cedergreen et al. (2008) reported additive effects with some compounds and in other cases found independent or synergistic effects. To simplify the difficulty of estimating combined toxicity, one approach to risk assessment (even with chemicals employing different modes of action) has been to use additive concentration related toxicity, such as TUs even though the assumption of additivity may not be true in all cases (Deneer 2000, Belden et al. 2007, Cedergren et al. 2008).

4.2 Pesticide concentration comparisons with other regions and land uses

California's Central Coast is a unique region ecologically and agriculturally, however some insight may be derived from examining pesticides detected in this study relative to those found by studies conducted in other regions, and in areas dominated by non-agricultural land uses. Pyrethroid detections in Central Coast sediments monitored for this study in May 2010 occurred in 70% of sites, compared with a Central Valley detection in 75% of sites in a 2002-2003 period study (Weston et al. 2004) and in 97% of sites west of the San Joaquin River and 48% of sites on the eastside of the San Joaquin in sediments collected in 2007 (Domagalski et al. 2010). The most commonly detected pyrethroid pesticide in this Central Coast CMP study was lambda-cyhalothrin, detected at 50% of sites sampled, whereas in the Central Valley the most commonly detected was permethrin, detected at 66% of sites (Weston et al. 2004). In the San Joaquin Valley the most commonly detected pyrethroid was bifenthrin, at 64% of sites (Domagalski et al. 2010). The highest concentration of permethrin found in the Central Coast was 286.4 ng/g compared with maximum detections of 129 ng/g in the Central Valley and 108 ng/g in the San Joaquin. Maximum concentrations of bifenthrin were 216.4 ng/g, 28.8 ng/g and 15.8 ng/g for the Central Coast, Central Valley and San Joaquin respectively. Highest concentrations of lambda-cyhalothrin were 22.0 ng/g, 16.8 ng/g and 19.8 ng/g for the Central Coast, Central Valley and San Joaquin respectively. Boxplots comparing median and maximum concentrations of four pyrethroid pesticides at sites demonstrating significant toxicity to *H. azteca* are displayed in Figure 13 for the Central Coast and Central Valley.

Pyrethroid and chlorpyrifos analysis in a study of Mississippi delta sediments from locations in Arkansas and Mississippi showed fewer detections compared with California's Central Coast. Of the five sites monitored 3 times in Mississippi, only 1 (and only on 1 of 3 monitoring events) had detected levels of chlorpyrifos, no sites had detections of bifentrhin, and lambda-cyhalothrin was detected at 1 site during 1 monitoring event (Lizotte et al. 2009).

A study by Amweg et al. (2006), focused on pesticides and toxicity of bed sediments in urban areas near Sacramento and the East San Francisco Bay cities, targeting sites with residential and mixed commercial and residential land uses. They found frequent pyrethroid detections of permethrin, cypermethrin, cyfluthrin and bifenthrin and reported toxicity for 67% of samples from urban Sacramento creeks and sloughs, and for 53% of samples from East Bay creeks. Cypermethrin and cyfluthrin ranged in concentration from 2 to 30 ng/g in sediments in their urban study compared with a range between 0 and 16 ng/g in this CMP study. Bifenthrin and permethrin were detected at greater than 75 ng/g in some CA urban sites, whereas in this CMP study detections of these pesticides were normally less than 30 ng/g however occasionally were greater than 200 ng/g. Chlorpyrifos was normally below 10 ng/g in the urban study with one detection at 92 ng/g; whereas in this CMP study its concentration generally was greater than 10 ng/g when it was detected, however the highest detected concentration was 63 ng/g. The site they characterized as most toxic due to the high mortality observed was a creek formed entirely by runoff from single family residences (Amweg et al. 2006). Because Central Coast subregions are mixed land uses, the source of pesticides at many CMP sites could be agriculture, commercial and/or residential. Further study would be required to assess the relative contribution of each to pesticides found in regional waterbodies. Although in California more pounds of pesticides are applied on agricultural land than in urban areas, agricultural users receive training in proper application, invest in management practices to reduce runoff, and are more closely regulated by the CA DPR (CA DPR 2009, CA DPR 2010). Homeowners, who do not receive this training, may not apply pesticides with the same care and precision. Efforts to reduce the number and concentration of pesticides found in regional waterbodies will necessarily include outreach to all user groups.

5 CONCLUSION

Sediments collected from rivers, tributaries and drains throughout much of the CMP monitoring area of California's Central Coast region show evidence of pesticide concentrations that are toxic to *H. azteca*.

Statistically significant toxic effects were observed in sediments from 28 of the 46 sites sampled (61%) for this study. Toxicity was evidenced by higher mortality compared with control test organisms at 27 sites and by lower growth at 1 site. Toxicity was not observed at the majority of the mainstem river sites sampled. Of the 10 river sites sampled, only the 3 furthest downstream Salinas River sites showed toxicity (309OLD, 309SAC, 309SSP). Toxicity in creeks (13 out of 20 sites) and irrigation drains (6 out of 8 sites) was more common, at 65% and 75% of sites in each category, respectively. Sediments from estuaries or sloughs were toxic to *H. azteca* at 5 out of 8 sites (62%). Survival rates for *H. azteca* tested in sample sediments were less than 85% compared with those in control sediments at 22 of 46 sites.

The majority of mortality observed in this study appears to be related to the concentrations of pesticides found in bed sediments. During this study, all sites (100%) with detections of individual pesticides above the 0.5 TU benchmark displayed statistically significant mortality to *H. azteca*. This result was similar to the findings of the Weston et al. (2004) study, which identified lethal effects in samples when an individual pyrethroid was greater than the 0.5 TU threshold, with a few rare exceptions. Of the 3 sites that did not have an individual pesticide concentration >0.5 TUs but had total added TUs >0.5, one showed significant mortality. Using the benchmark >0.5 TUs, an individual pesticide could have explained toxicity in 70% of sites in this study which demonstrated survival related toxicity to *H. azteca*. It is unknown what contributed to the mortality in the 8 samples which showed a significant toxic effect but had less than 0.5 TUs of detected pesticides. In these cases unexplained toxicity could have been associated with interactive effects among pesticides, toxicants not analyzed, non-homogeneity of sample sediments, or other factors.

The frequency of detection and concentration of pesticides found in bed sediments in Central Coast CMP waterbodies during this monitoring event may affect aquatic life beneficial uses. The benthic invertebrate *H. azteca* showed significantly reduced survival rates (in laboratory toxicity tests), and reductions in survival in most cases co-occurred with pesticide concentrations at known lethal levels, found in sediments from those sites. Although the effect of observed concentrations on the survival of other resident species is unknown, their survival may be potentially be affected directly by the pesticides or indirectly by structural changes in the food web as a result of altered or reduced invertebrate populations.

Not all subregions in the CMP study area have uniform pesticide concentrations or toxicity to *H. azteca*. Results from this study indicate that sites monitored in the San Luis Obispo, Santa Ynez and Pajaro River watersheds showed fewer toxic effects to the survival or growth of *H. azteca* compared with Santa Maria, Salinas, and Santa Barbara. Decreased survival rates generally coincided with increased concentrations of pesticides, however there were a few exceptions. Notably, two sites near Carpinteria (Franklin Creek (315APF) and Arroyo Paredon (315APF)] showed mortality, but pesticides were not detected at Arroyo Paredon, and were found only in low concentrations (0.11 total added TUs) at Franklin Creek, perhaps implicating other toxicants. No pesticides were analyzed at concentrations greater than 0.5 TUs in the San Luis Obispo, Santa Barbara or Santa Ynez regions. Two sites in the Pajaro watershed (20% of sites) had concentrations in excess of 0.5 TUs for one or more pyrethroids, but chlorpyrifos was not detected at any Pajaro watershed sites. Eight sites on Salinas waterbodies (50% of sites) and eight sites in Santa Maria (89%) had pyrethroid concentrations greater than 0.5 TUs. Chlorpyrifos was detected at concentrations greater than 0.5 TUs at five sites in Salinas (31%) and at all nine sites in Santa Maria (100%); however was not detected above this benchmark in other subregions.

This study has not included a source analysis of the origin of pesticides that were detected. While pyrethroids are used on crops for pest control, they are also used in residential homes and gardens, for commercial landscape maintenance, and for structural pest control applications. Although agricultural and professional applications to commercial properties or residences require submission of use information (including active ingredient, amount applied, date of application, acreage treated, location, and crop or site treated) to the California Department of Pesticide data base (www.cdpr.ca.gov),

homeowners are not required to submit pesticide use information. In the mixed use landscape of the Central Coast, finding ways to reduce all potential sources is important to any effort to reduce the frequency and concentration of pyrethroids and other pesticides in the environment.

It is also important to note that the CMP has not conducted any studies to examine a causal link between pesticides in sediment and observed toxicity. Though this study suggests a strong link, as all samples with > 0.5 TUs related to any single pesticide were toxic and 100% mortality (0% survival) was observed in all samples where either or both chlorpyrifos or added pyrethroids TUs > 2.1. However as there was also evidence of toxicity where lower pesticide concentrations were detected, it is important to consider other toxicant classes as well.

As with prior studies, results from this study will be used in outreach efforts to farmers, agricultural trade associations, pesticide manufacturers, and crop production service providers. Cooperative Monitoring Program staff present sediment pesticide data together with corresponding toxicity data, and in comparison to published LC_{50} values. Results are also presented in the context of RWQCB 303d-listing criteria for the protection of aquatic life. Emphasis is placed on presenting locally relevant data, which is essential to grower management efforts.

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