

Aquatic Pesticide Monitoring Program

Aquatic Pesticide Monitoring Program Final Report

**Geoffrey S. Siemering
Jennifer Hayworth
Aroon Melwani**

SFEI Contribution 392
February 2005

San Francisco Estuary Institute



Aquatic Pesticide Monitoring Program

Final Report

Geoffrey S. Siemering

Jennifer Hayworth

Aroon Melwani



San Francisco Estuary Institute
7770 Pardee Lane, 2nd Floor
Oakland, CA 94621

February 2005

This report should be cited as;

Siemering, G., Hayworth, J., and Melwani, A. 2005. Aquatic Pesticide Monitoring Program Final Report. SFEI Contribution Number 392. San Francisco Estuary Institute, Oakland, CA.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	1
INTRODUCTION.....	5
BACKGROUND.....	5
MANAGEMENT AND ASSESSMENT QUESTIONS.....	7
ORGANIZATION.....	9
MONITORING PROGRAM.....	11
TARGET PESTICIDES.....	11
SITE SELECTION.....	13
SAMPLING STRATEGY	14
ANNUAL GOALS.....	15
REFERENCE LOCATIONS.....	17
SAMPLE COLLECTION METHODS	20
DATA MANAGEMENT.....	20
APPROACH TO RISK ASSESSMENT.....	21
<i>Sediment Quality Triad Approach</i>	21
<i>Risk Quotient Calculation</i>	22
RESULTS	24
2,4-D	24
COPPER SULFATE.....	27
CHELATED COPPER	32
DIQUAT DIBROMIDE	34
FLURIDONE	36
GLYPHOSATE	40
METHOPRENE	41
TRICLOPYR	43
CONCLUSIONS	44
MANAGEMENT AND ASSESSMENT QUESTIONS REVISITED.....	48
REFERENCES.....	50

LIST OF TABLES

Table 1. Steering Committee Organization Member List.....	10
Table 2. Science Advisory Committee Members	10
Table 3. Pesticide Ranking Table	13
Table 4. Sampling frequency, collection order, and locations.....	18
Table 5. APMP Sampling Sites	18
Table 6. Threshold Values Applied in Chemistry Evaluation.....	22
Table 7. Aquatic Animal and Plant Levels of Concern	23
Table 8. Peak Concentration Risk Quotient Calculations for 2,4-D Application.....	25

Table 9. Peak Concentration Risk Quotient Calculations for Surfactant (R-11) during 2,4-D Application.....	25
Table 10. Sediment Quality Trend Calculations for 2, 4-D (DMA).....	26
Table 11. Summary of 2, 4-D (DMA) Sediment Quality Trend Data	26
Table 12. Water Risk Quotient Calculations for Copper Sulfate Applications (Reservoir System)	27
Table 13. Sediment Quality Trend Calculations for Copper Sulphate	29
Table 14. Summary of Copper Sulphate Sediment Quality Trend Data.....	30
Table 15. Water Risk Quotient Calculations for Chelated Copper Applications (Irrigation Canal Systems).....	32
Table 16. Sediment Quality Trend Calculations for Chelated Copper	33
Table 17. Summary of Chelated Copper Sediment Quality Trend Data	33
Table 18. Water Risk Quotient Calculations for Diquat Dibromide Applications	35
Table 19. Peak Risk Quotient Calculations for Fluridone Application at MID Main Canal	37
Table 20 Sediment Quality Trend Calculations for Fluridone.....	38
Table 21 Summary of Fluridone Sediment Quality Trend Data.....	38
Table 22. Risk Quotient Calculations for Surfactant (R-11) during Glyphosate Application at Doris Drain.....	40
Table 23. Peak Concentration Risk Quotient Calculations for Methoprene Application.	42
Table 24. Risk Quotient Calculations for Surfactant during Triclopyr Application.....	44

LIST OF FIGURES

Figure 1. APMP Sampling Locations.	19
Figure 2. Typical Sampling Plan for an Individual Site	20

EXECUTIVE SUMMARY

The APMP collected data during three aquatic pesticide application seasons which indicated that widespread acute ecosystems impacts will not occur from aquatic pesticides applied according to their label requirements. However, risk quotient exceedances and sediment quality triad calculations indicate that significant questions remain concerning potential localized acute impacts and chronic impacts. For most pesticides, further risk characterization is indicated.

Additionally, surfactants (frequently added to pesticides by the applicator immediately prior to application) may be an order of magnitude more toxic than the active ingredient pesticide and may possibly be endocrine disrupting substances. Little information is required for registration of surfactants by either U.S. EPA or California Department of Pesticide Regulation. In some cases, surfactants of the same chemical class are sold premixed with the active ingredient pesticide for terrestrial formulations, but for aquatic uses the surfactant is removed from the product. There is a significant need for additional risk characterization of surfactants.

The three years of data gathered by the APMP should only be used for screening purposes in order to identify where further risk characterization or research may be needed. Definitive conclusions cannot be drawn from this data due to the small sample number, the variety of application scenarios, and the disparate water body types monitored. APMP generated chemical characterization, toxicity, and bioassessment data. The chemical characterization and toxicity data generated can be used for screening purposes. In complex field situations, bioassessments require multiple years of data before preliminary conclusions can be drawn from them. Concurrent data collection and analysis of all three data types (chemical, toxicity, and biological) provides important integrative information for ecosystem risk evaluation.

Specific conclusions concerning individual pesticides:

2,4-D

Monitoring of 2,4-D (in the 2,4-D dimethylamine salt formulation) with added surfactant showed no toxicity to the three standard EPA species nor did risk quotients

indicate the need for further information. Vitellogenin induction laboratory experiments indicated that 2,4-D may cause endocrine disruption at legal application rates.

The vitellogenin induction studies indicated the need for further study of the aquatic 2,4-D formulations and their primary breakdown products. This level of research should not be expected from entities conducting compliance monitoring.

Acrolein

Because of acrolein's rapid volatilization, work focused on development of a field sampling method that would allow for accurate determination of the pesticide in water. Current standard environmental sampling methods are inadequate for sampling of acrolein treated water and result in unreliable analytical results.

Refinement of the sampling methodology began in 2003. Results indicated that the method developed performs well at low acrolein water concentrations, making it possible to determine acrolein residue values.

Due to acrolein's rapid volatilization, it is currently not possible to conduct standard water toxicity tests on it. Because of its' extremely low Lowest Observable Effect Concentration (LOEC) values, the detectable presence of acrolein indicated that very high mortality to EPA water and sediment toxicity test species can be assumed.

The development of diagnostic response tests (i.e. phytomonitoring, sentinel bivalves and fish, etc.) were explored and additional work is warranted. These tests have the potential to provide a low cost, low tech method of detecting acrolein outside of designated treatment areas.

Copper Sulfate

Copper sulfate applications were monitored in three reservoirs. Toxicity to juvenile trout and Ceriodaphnia following application was observed. Peak concentration risk quotients showed acute and chronic U.S. EPA Office Pesticide Programs Levels-of-Concern (LOC) exceedances.

In the reservoir treated with granular copper sulfate applications, significant mortality was observed in Ceriodaphnia and juvenile trout water toxicity tests immediately after application within the treatment area. Mortality and growth inhibition

was also observed in a number of the sediment samples. Sediment copper concentrations at many sites exceeded a published *Hyallela azteca* LC50 value. However, the variable toxicity results observed in the sediments indicates that the majority of the copper is not bioavailable.

These findings indicate the need for further risk characterization associated with copper sulfate applications.

Chelated Copper

Chelated copper pesticides were monitored during applications in two irrigation canal systems. One system used a product of mixed copper ethanolamines and the other the same product of mixed copper ethanolamines in an emulsified formulation. Chelated copper formulations are likely to have distinct behavior from each other and copper sulfate in aquatic environments based on the chelating agent as well as other adjuvants. It should be noted that copper carbonate is the active ingredient in other chelated copper pesticide products and no monitoring of copper carbonate based pesticides was conducted.

In both systems, the water samples were similarly toxic both before and after application. Therefore, no definitive conclusions can be drawn about the toxicity of mixed copper ethanolamines. The sediment quality triad calculations indicate the possibility of copper impacts to the system.

Further risk characterization associated with chelated copper applications is warranted.

Glyphosate

Glyphosate was monitored at several locations. No toxicity was found to be associated with glyphosate applications. Glyphosate is often applied with a surfactant, which may have much higher toxicity than the active ingredient.

Based on risk quotient calculations and toxicity data, no further risk characterization associated with glyphosate only applications is warranted. Risk characterizations are warranted when a surfactant is used in conjunction with the glyphosate.

Diquat Dibromide

Diquat dibromide was sampled at two locations, one small pond and a Delta slough. Diquat risk quotients similarly exceeded Levels-of-Concern at all sampling periods in the Delta slough (including pre-application) and at one hour after application in the pond. Diquat may be applied with a surfactant which may exhibit much higher toxicity than the active ingredient. Diquat sediment concentrations were not considered as diquat is irreversibly adsorbed to sediments and is thereafter not bioavailable.

Toxicity test and risk quotient results indicate the need for further risk characterization.

Fluridone

Fluridone (applied in pellet or liquid form) was not found to be definitively toxic to or have Levels-of-Concern (LOCs) exceedances for the three standard U.S. EPA species for water or sediment amphipod organisms. The peak concentration risk quotient for Stonewort did exceed an acute LOC. Fluridone was found to cause sublethal toxicity (decreased shoot and root length) to *Typha latifolia*. This would indicate a potential for impacts to non-target plants.

Further risk characterization of fluridone impacts on non-target plants is warranted. There is also cause for concern over development of genetic resistance to fluridone which is emerging in plant populations in Florida.

Methoprene

Monitoring for methoprene is challenging because it is commonly applied to environments that do not lend themselves to traditional water and sediment sampling and testing methods. These systems usually have extremely shallow water and highly anoxic sediments which impede standard toxicity tests. *In-situ* and laboratory toxicity tests were completed, but the results were inconclusive. From the one site monitored for methoprene, water and porewater risk quotients did not exceed criteria. However, further risk characterization is needed. Methoprene was persistent for several weeks in marsh sediments up to the ppm level. Little methoprene sediment toxicity data could be located in the literature.

Future work is warranted to further characterize the risk of methoprene in sediments. Additional studies may also be warranted due to the common simultaneous application of methoprene and *Bacillus Thuringiensis israelensis* (BTi).

Triclopyr

Triclopyr (in the triclopyr, triethylamine salt formulation) was monitored at one location. Triclopyr peak concentration risk quotients showed no Levels-of-Concern exceedances. Triclopyr is often applied with a surfactant, which may exhibit higher toxicity than the active ingredient. Further risk characterizations are warranted since a surfactant was used with triclopyr.

Nonionic surfactants

The most commonly used surfactants at APMP monitoring sites were Target Prospread Activator and R-11. Both are nonylphenolethoxylate based surfactants. Peak concentration risk quotients indicated Levels-of-Concern exceedances for a wide range of animal species including Delta Smelt and Sacramento Splittail. Vitellogenin induction experiments in Rainbow trout indicated that these nonylphenol surfactants can be an endocrine disruptor at application rates. There are a wide range of surfactants available, each one having a different toxicological profile. Due to their classification as an adjuvant, very little data is required for registration. However, our results suggest that further risk characterizations are warranted for all surfactants.

INTRODUCTION

Background

In January 2002, the San Francisco Estuary Institute (SFEI) began the development and implementation of a statewide aquatic pesticide monitoring program (APMP) with funding from the California State Water Resources Control Board (SWRCB). The APMP was funded to evaluate the potential water quality impacts associated with the application of aquatic pesticides because of a series of court decisions and a legal settlement. Aquatic pesticides fall into two distinct groups, herbicides and mosquito vector control compounds. These are compounds that have registration labels that explicitly allow direct application to waterbodies. Pesticides applied for terrestrial

use that reach waterbodies (i.e. through runoff or spray drift) were not studied as part of this project.

In 2001, a ruling by the U.S. Ninth Circuit Court of Appeals, in *Headwaters, Inc. v. Talent Irrigation District*, stated that registration and labeling of aquatic pesticides under the federal pesticide law (Federal Insecticide, Fungicide, and Rodenticide Act or FIFRA) does not preclude the requirement to obtain coverage under a National Pollutant Discharge Elimination System (NPDES) permit prior to discharging such pesticides into waters of the United States (243 F.3d 526 (9th Cir. 2001). *Headwaters, Inc. v. Talent Irrigation District*, the U.S. Court of Appeals for the Ninth Circuit). The SWRCB issued an emergency NPDES permit in July 2001. This permit was challenged in California state court by the environmental advocacy group Waterkeepers of Northern California on the grounds that it did not provide sufficient protection of the environment (*Waterkeepers Northern California v. State Water Resources Control Board*, Alameda County Superior Court No. 2001-022050). This legal challenge coupled with that of the *Talent* decision rendered the legal application of aquatic pesticides in California impossible for the 2001 application season (generally April-September). This legal challenge was settled with an agreement that the SWRCB would fund aquatic pesticide research and monitoring to provide the state with rigorously reviewed scientific information to develop an acceptable general NPDES permit upon expiration of the emergency permit in January 2004. In the settlement, SFEI, a non-profit organization with a Board of Directors including scientists, environmentalists, regulators, and dischargers to the Bay, was designated as the scientific entity responsible for the implementation of the APMP. The settlement mandated that \$1,950,000 be spent on aquatic pesticide monitoring and research and \$600,000 exploring nonchemical alternatives to the use of aquatic pesticides. The contract funding this program states that,

“the objective of the APMP is to implement comprehensive monitoring and special studies to evaluate the water quality impacts associated with the application of aquatic pesticides and the non-chemical alternatives to the use of aquatic pesticides. The primary focus shall be to provide information to the SWRCB and Regional Water Quality Control Boards (RWQCBs) to enable to SWRCB and RWQCBs to effectively regulate discharges of aquatic pesticides to surface waters.”

In addition, the contract with SFEI specified that the follow studies be undertaken:

1) Fate and transport of applied materials and breakdown products, including residence time in the environment, mass loading of the pesticide, and evaluation of bioaccumulation.

2) Assessment of impacts to beneficial uses including: potential routes of exposure, life cycle bioassessments on a range of species, biochemical and/or physiological testing of sublethal effects including reproduction and growth.

3) Characterization of accumulation in sediments where a pesticide is suspected of sediment accumulation.

4) Characterization of accumulation in organisms where persistence or bioaccumulation is suspected.

5) Conduct community monitoring surveys including evaluation of nontarget plants or animals, organism diversity and ecosystem integrity.

Management and Assessment Questions

While the legal settlement and initial contract gave general guidance, the exact nature of the monitoring and research efforts were not detailed. To help direct the monitoring effort development, Management and Assessment questions were derived at the outset of the APMP. Management questions are overarching questions that need to be answered in order to accomplish the project goals. Assessment questions are second tier questions that address specific knowledge items that need to be determined to adequately answer the Management questions. This Management and Assessment question model for developing the program was used in order to provide a theoretical framework that would keep the scientific work on track. These questions were referred to throughout the project at all stages of planning and development.

The Management and Assessment questions developed for the APMP are as follows (management questions in italic):

1. *Which aquatic pesticides used in California have the highest “risk” of impacts to people and the environment?*

Aquatic Pesticide Monitoring Program
Final Report

- a. What is the amount of each aquatic pesticide used?
 - b. What is the aquatic toxicity of each compound?
 - c. Where are the compounds being used?
 - d. When are the compounds being used?
 - e. What is their environmental fate and persistence?
2. *What are the concentrations of the target aquatic pesticides in the environment (water, sediment, and biota) adjacent to their application point?*
- a. What are the concentrations in the dissolved fraction and particulate fraction (45 micron) of water?
 - b. What are the concentrations in sediment pore water?
 - c. What are the concentrations in bulk sediments?
 - d. What are the concentrations in the gonads of native fish?
 - e. What are the concentrations in the muscle tissue of native fish and bivalves?
 - f. Are there wet-dry seasonal differences in concentrations?
3. *Are the measured concentrations above existing effects thresholds?*
- a. Is the water or sediment toxic using Standard Bioassay Protocols?
 - b. Are there human health risks associated with water contact or eating fish or shellfish?
4. *Which locations have the highest “risk” of beneficial use impairment?*
- a. Should a sample of systems using pesticides be monitored?
 - b. Are there sensitive areas (i.e. wildlife refuges, wilderness areas, etc) particularly at risk?
5. *What is the degree of biological impacts to non-target biota from application and exposure to aquatic pesticides?*
- a. Are population mortality rates elevated compared to a reference population in ‘clean’ waters?
 - b. Is growth impaired?
 - c. Is reproduction impaired?

The Management and Assessment questions, generated through numerous discussions, were used to develop a plan of action for monitoring aquatic pesticide use.

The monitoring plan ultimately developed attempted to address as many of the assessment questions as possible within the fiscal and logistical constraints of the project.

Studies used to evaluate potential pesticide impacts will hereafter be referred to in general as monitoring. The term monitoring to many in the scientific community means to test or sample on a regular or ongoing basis. However, to avoid overly length descriptive terms for the various studies conducted, this report will use the word monitoring to mean “to keep track of systematically with a view to collecting information.” The ‘monitoring’ performed during the APMP could be more precisely described as case study investigations performed with a wide variety of scientific tools to help inform the development of aquatic pesticide NPDES permits.

Organization

Due to the politically charged environment, SFEI established a consensus-building, stakeholder-driven process to oversee the work. By having all interested parties involved from the inception of the project and giving input throughout, it was possible to achieve acceptance both of the methods used and data generated from the project.

To ensure scientific rigor, an external scientific peer review committee was established to provide review and guidance for the project. Several focused workgroups were formed to address questions relating to chemistry, toxicity, modeling and bioassessments. The members of these workgroups were drawn from local academic institutions, government laboratories, and private firms. Contract laboratories were identified to perform the sample testing necessary. A mixture of university, government, and private labs were selected according to their expertise.

Since the driving impetus for this project came from within the legal system, a project Steering Committee composed of individuals from Federal and State agencies, stakeholder groups, and public interest groups was assembled (**Table 1**). Early in the project, the monthly steering committee meetings focused on creating an organizational structure for the APMP and guiding the development of the monitoring plans, later quarterly meetings focused on discussing and resolving programmatic development issues. The meetings were open to all interested parties as well as steering committee members.

Aquatic Pesticide Monitoring Program
Final Report

Table 1. Steering Committee Organization Member List

Central Valley Regional Water Quality Control Board	California Farm Bureau Federation	California Department of Fish & Game
U.S. Dept. of Agriculture	Monsanto	Contra Costa Mosquito Vector Control District
South San Joaquin Irrigation District	DeltaKeeper	U.S. Fish & Wildlife Service
U.S. EPA, Region 9 (WTR 5)	Syngenta	National Marine Fisheries Service
Association of CA Water Agencies	Ventura County Water Protection District	Orange County Public Facilities Department
Bay Area Stormwater Management Agencies Association	San Joaquin County Mosquito Vector Control District	EMC Environmental Consulting Services.
California Dept. of Pesticide Regulation	Metropolitan Water District of Southern California	Solano Irrigation District
California Dept. of Boating and Waterways	Marin Municipal Water District	State Water Resources Control Board
San Francisco Baykeeper	Sutter County Agriculture	California Dept of Health Services Vector-Borne Disease Section
Los Angeles Dept of Water & Power	Marin Municipal Water District	California Dept of Food and Agriculture
U.S.EPA, Region 9	California Water Quality Coalition	

The external peer review panel, hereafter referred to as the Science Advisory Committee (SAC), was composed of five scientists who are recognized as experts on pesticides and their effects. This committee provided independent peer review for APMP workplans and findings. This committee met at the outset of the project and then annually to review the results and upcoming plans. The SAC members were also consulted periodically as technical questions arose and received written updates quarterly. SAC members are listed in **Table 2**.

Table 2. Science Advisory Committee Members

Name	Affiliation
John H. Rodgers	Clemson University Institute of Environmental Toxicology
Lenwood Hall	University of Maryland Agricultural Experiment Station Wye Research and Education Center
Michael Anderson,	University of California-Riverside Department of Environmental Sciences
Jay Gan.	University of California-Riverside Department of Environmental Sciences
R. David Jones	U.S. Environmental Protection Agency Office of Pesticide and Toxic Substances

MONITORING PROGRAM

The monitoring program that SFEI was charged with implementing was intended to have wide spatial coverage, to investigate behavior of all pesticides currently in use in California, determine potential impacts in the range of waterbody types receiving applications, and provide information on aquatic pesticides free of any additional confounding factors. It was agreed upon early in the program, that the length of time allowed and the funding provided were insufficient to accomplish the three goals. A tiered approach was developed to achieve a balance between program goals and what was practically achievable. In addition, ranking schemes and selection criteria were developed to guide site selection, pesticide priority, and monitoring methods.

The tiered approach that helped focus the implementation of the aquatic pesticide monitoring efforts is as follows:

Tier 1. Information-based research. Conduct a literature review to identify likely pesticide/environmental couplings where accumulation is likely or unlikely, determine annual usage from California Department of Pesticide Regulation database, and develop a permit holder database to identify best possible candidate monitoring sites

Tier 2. Field monitoring. Conduct sampling to confirm presence or absence of pesticide in aquatic ecosystems, potential water and sediment toxicity, and impacts to non-target invertebrate populations.

Tier 3. Special studies. Where tier 1 & 2 results indicate, conduct special projects to address technical sampling issues or more fully characterize specific aquatic pesticide environmental impacts.

Target Pesticides

Potential target pesticides were ranked based on the following criteria: aquatic uses, amount used, common usage, toxicity/risk, public concern, reliable analytical methods, and regulatory significance (Table 3). Information on these aquatic pesticides was collected through a detailed literature review conducted by SFEI (Siemering et al.

Aquatic Pesticide Monitoring Program
Final Report

2003), from the California Department of Pesticide Regulation Pesticide Use Report database, and from the professional opinions of a subset of steering committee members.

The mosquito vector control compounds were generally not addressed by the APMP due to the difficulty in finding suitable sampling locations, the lack of adequate analytical methods, and infrequent or “emergency” use of many compounds. The three primary mosquito control insecticides used are *Bacillus Thuringiensis israelensis* (BTi), methoprene and larvicidal oils. There are no standard analytical methods for BTi and no toxicity test methods for methoprene, due to its rapid degradation. Larvicidal oils vary in content and are also similar to other petroleum products frequently found in the environment.

Aquatic Pesticide Monitoring Program
Final Report

Table 3. Pesticide Ranking Table

Chemical	Selec- tivity	Toxicology				Phys Chem			Perception	Total Score	Final Rank
		Indirect	Ecosystem	Terrestrial	Human	Half -life	Kow	Mobility			
1 – low risk 5 – high risk										Sum of criteria scores	
Acrolein	5	4	5	2	(4)	1	1	5	5	32	1
Copper (total and ionic)	2	4	4 - 5	1 – 2	1	2 ¹	2	2 – 3	5	26	2
2,4-D (salt)	1	(3)	2 - 3	1 – 2	1	2	3	2	3 – 4	20	3
Endothal	2	4	2	1	(1)	2	(3)	(3)	2	19	4
Fluridone	3	2	1	1	1	3	2-3	3	1 – 2	19	4
Triclopyr	1	4	2	1	(1)	2	(3)	(3)	3 – 4	19	4
Diquat dibromide	3	4	2 - 3	1	1	1	1	1	3	18	5
Glyphosate	5	1	1	1	1	1	1	1	(4)	16	6

¹Bioavailable form
() estimated values

Site Selection

The regulatory areas that were considered for sampling included irrigation supply systems, drinking water reservoirs, exotic weed control (canals and coastal), flood control and drainage, and storm water and recreational impoundments (golf courses and parks). A ranking system was developed with regard to system complexity. Monitoring was conducted in increasingly complex water bodies as sampling methods, staff experience and site knowledge were developed to adequately accommodate the specific system characteristics. The complexity of water systems were ranked as follows (in order of increasing complexity): irrigation district canals < storm water canals and small streams < lakes or reservoirs < Sacramento/ San Joaquin Delta < San Francisco Bay or other coastal estuaries.

Within each water body category, the sampling sites selected for monitoring were based on the following criteria:

1. Representative of typical applications of identified pesticide of interest,
2. Limited, or well-characterized inputs,
3. Existence of chemical analysis methods with detection limits sufficient for ambient environmental monitoring,

4. Representative of a typical application by a pesticide user group (e.g., a municipal drinking water district, a irrigation district, a county public works department, and county agriculture office).

In 2002, a database of aquatic pesticides NPDES permit holders was created. From this database, individual permit holders were identified for water bodies that would provide the greatest amount of spatial coverage and represent the greatest number of user groups and pesticides. These permit holders were then contacted to ascertain interest in collaborating with APMP and to gather further details on the systems receiving applications. Only one permit holder was not willing to participate. The final site selections were made after site evaluations by APMP staff. While APMP sampled the largest number of sites possible, there was a large disproportion relative to the total number of sites receiving aquatic pesticide applications within California.

SAMPLING STRATEGY

Combining the assessment questions with the tiered approach and ranking criteria, the specific APMP monitoring objectives at each sampling site were to:

1. Determine fate and transport of applied chemicals.
2. Evaluate the acute lethal effects of pesticides on aquatic organisms through toxicity testing.
3. Evaluate the sublethal effects of pesticides on aquatic organisms. This entailed assessment of potential biochemical and/or physiological effects by toxicity testing.
4. Evaluate the effects of pesticides on non-target aquatic biological communities.
5. Determine the effect of repeated pesticide exposure on benthic macroinvertebrates. Community structure elements included taxonomic, functional, and tolerance composition, along with abundance and diversity measures.
6. Determine the effects of pesticide applications on the benthic macrophyte community and associated epiphytic macroinvertebrates. Effects could include

pesticide drift and changes in water column chemistry from decomposition of aquatic vegetation. Community structure elements were assessed for benthic macrophytes include taxonomic composition, frequency distribution, coverage, abundance, and diversity measures. Epiphytic macroinvertebrates were analyzed for the same community structure elements as the benthic invertebrates.

7. Determine the effect of pesticide exposure on phytoplankton communities. Community structure elements that were assessed include taxonomic composition, abundance, and diversity measures.

Annual Goals

In 2002, the first year of the project, the sampling was mandated by the legal settlement to begin no later than July 1st. To accomplish that goal, sampling was limited to preliminary studies of pesticide fate at selected sites for high priority pesticides. Measurements included chemistry, water, tissue and sediment sampling.

Year two incorporated a triad sampling approach recommended by the EPA (Barbour et al., 1999). This included synoptic sampling for chemistry, toxicity, and biological assessments data. Bioassessments focused on communities that are widely recognized as appropriate biological indicators of contaminant impacts: aquatic macroinvertebrates, macrophytes, and algal communities (U.S. EPA, 2003). Due to the diverse nature of the target pesticides and water-body types studied, the type of bioassessments conducted were specifically adapted for each pesticide sampling event. However, where possible all studies were similarly designed and the data obtained was directly comparable. The specific goals for the 2003 monitoring effort were: 1) to revisit appropriate sites studied in Phase 1, 2) perform chemical analysis and toxicity testing for all pesticides of interest, 3) expand the number of study sites, 4) implement bioassessment studies all locations, and 5) begin special studies to fill gaps in knowledge of target pesticide and selected adjuvant (surfactants) behavior.

Efforts in 2004 focused on special studies to answer questions raised during the first two years. The primary focus of these studies was non-target organism impacts and potential long term impacts.

It was decided that APMP's monitoring goals would be most efficiently achieved by closely coordinating with current aquatic pesticide users during their pesticide application cycle. By closely tying the sampling events to a pesticide application, 'worst-case' scenarios could be investigated. Given the limited time and budget of the APMP, looking at such worst-case scenarios was felt to be a prudent approach. During years two and three, the 'worst-case' regime was augmented with longer term macroinvertebrate and phytoplankton bioassessment studies. These bioassessment studies allowed for a more comprehensive investigation into potential environmental impacts (chronic and acute) of aquatic pesticide applications.

This "worst-case scenario" design explored the fate of pesticides applied at normal field concentrations and yielded data on both acute and longer term pesticide impacts. The sampling frequency enabled detection of potential biological responses as macroinvertebrates, and to a lesser extent, phytoplankton and macrophytes responded to a perturbation.

A diverse range of water-body types located throughout California were monitored. The frequency and level of sampling varied because of pesticide and site-specific issues (e.g. presence of other potential contaminants, availability of reference sites). The pesticides monitored included acrolein, 2,4-D (dimethylamine), copper sulfate, chelated copper (copper ethanolamine), diquat dibromide, fluridone, glyphosate, methoprene, and triclopyr (triethylamine). Due to the extremely volatile nature of acrolein, sampling of this contaminant focused on developing field sampling methods to account for this volatility. Endothal was initially identified as a pesticide of interest, however, due to its limited use in California, no monitoring was conducted.

A temporally stratified study design was implemented to coincide with pesticide application events. Samples were collected before pesticide application and at various increments after application (**Table 4**). We conducted quantitative sampling to enable spatial and temporal statistical comparisons. Sampling locations throughout the state are shown graphically in **Figure 1**. A graphic representation of sampling at a single site is shown in **Figure 2**. **Table 5** is a complete list of all sample locations.

Reference Locations

At each location where monitoring took place, a reference site was identified. The ideal reference site would have been an identical water body immediately adjacent to the treated water body that had never received applications. The Marin Municipal Water District reservoirs were closest to this ideal situation.

The sites selected as reference sites were as similar as possible to the treated sites without the application of pesticide. In flowing water bodies, this was often immediately upstream of a treatment area. In lentic systems, an untreated portion of the water body was selected. As with the treated sites, these reference sites often received input from sources possibly containing contaminants in addition to the aquatic pesticide applied. Every attempt was made to select sites with minimal uncharacterized inputs. These sites served as reasonable reference locations for the chemistry and toxicity studies.

However, for the benthic invertebrate studies, these reference sites were far from ideal. Most of the systems in California to which aquatic pesticides are applied are man-made, heavily altered, or highly impacted. Sites that would have been representative of minimally disturbed benthos were often remote and dissimilar to water bodies receiving treatment.

Aquatic Pesticide Monitoring Program
Final Report

Table 4. Sampling frequency, collection order, and locations.

Sample collection frequency
Pre-application
Initial Post-application (within 1-24 hrs) ¹
2 weeks post
4-6 weeks post ²
Order of Sample Collection
1. Physical Habitat Assessment
2. Water Quality Parameters
3. Macrophyte Survey
4. Sediment Parameters
5. Macroinvertebrate Assessments

¹ Macrophytes and macroinvertebrates not collected at this time.

² For long-term sampling of copper sulfate, fluridone, and glyphosate only.

Table 5. APMP Sampling Sites

Sampling Sites
<i>Cooperating Permit Holder /Treated Sites /Control Site / Pesticide</i>
Marin Municipal Water District / Bon Tempe and Nicasio Reservoirs / Lake Lagunitas / copper sulfate ¹
Cal. Dept. of Food and Agriculture / Costa Ponds / untreated pond / liquid fluridone ¹
U.S. FWS and Dept. of Boating and Waterways / Lower Stone Lake / Upper Stone Lake / glyphosate ¹
Sand Bay Isle Homeowners Association / Sand Bay Isle Ponds / diquat dibromide and copper sulfate
U.S. FWS and Dept. of Boating and Waterways / treated Stone Lake slough / untreated slough / 2,4-D
Solano Irrigation District / Byrnes canal / untreated canal section / chelated copper
Potter Valley Irrigation District / treated canal / untreated canal section / chelated copper
Big Bear Municipal Water District / treated lake area / untreated lake area / pelleted fluridone
Merced Irrigation District / Atwater Canal / untreated canal section / glyphosate
Merced Irrigation District / Main Canal / untreated canal section / liquid fluridone
Merced Irrigation District / LeGrande & Planada Canal / untreated canal section / acrolein
Merced Irrigation District / Livingston Canal / untreated canal section / acrolein
Ventura County Flood Control District / Doris Drain storm water canal / untreated section / glyphosate
Cal. Dept. of Food and Agriculture / Bear Creek / untreated creek section / triclopyr
Dept. of Boating and Waterways / Delta 7 Mile slough / untreated slough area / diquat dibromide
Cal. Dept. of Food and Agriculture / Clear Lake / untreated lake portions / pelleted fluridone
Cal. Dept. of Food and Agriculture / Anderson Pond / pretreatment / triclopyr
Contra Costa Mosquito VCD / Swanton's Marsh / untreated marsh area / methoprene

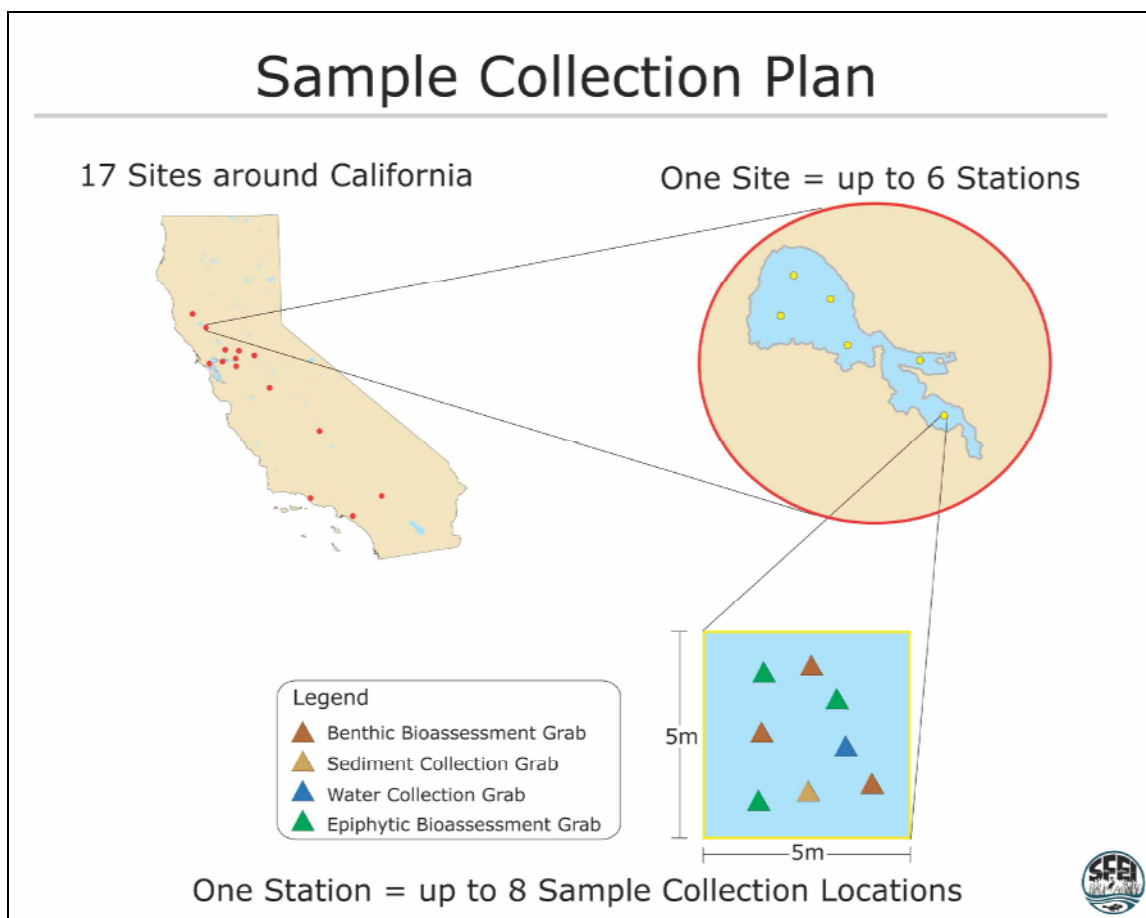
¹ Long-term study sites.

Aquatic Pesticide Monitoring Program
Final Report

Figure 1. APMP Sampling Locations.



Figure 2. Typical Sampling Plan for an Individual Site



Sample Collection Methods

Standard protocols for chemistry and toxicity sampling and handling have been compiled in the Aquatic Pesticide Monitoring Program Quality Assurance Project Plan (QAPP) (Yee *et al.* 2004). This document was reviewed by the U.S. EPA Region 9 Quality Assurance office. The bioassessment methods and results are detailed in Hayworth *et al.* 2004. These methods follow those developed by the California Department of Fish and Game and were adapted for the specific systems being monitored.

Data Management

All digital data and information generated from sampling are stored at SFEI in a California State Water Resource Control Board Surface Water Ambient Monitoring

Program (SWAMP) format. All data and reports are publicly available at SFEI's website.

Approach to Risk Assessment

Chemical characterization, toxicity tests and benthic and epiphytic test results were reviewed for trends that may indicate impacts due to aquatic pesticide applications. When sufficient data were available, we used the sediment quality triad approach for evaluating pesticide-contaminated sediments proposed by Chapman et al. (1991) and used in Canfield et al. (1994). In some cases, there was insufficient data to perform sediment quality triad calculations. In these cases, risk quotients were calculated for a range of test species. Where discrepancies occurred, they are highlighted in the text. The ultimate goal of this data interpretation is to identify areas that may need regulatory attention or additional research. However, these results in and of themselves can not provide definitive information on a particular pesticide's behavior in the environment.

Sediment Quality Triad Approach

The triad approach is an effects-based approach that integrates measures of chemistry, sediment toxicity, and benthic community structure, to evaluate sediment quality in aquatic and marine systems. Metrics used to evaluate chemistry were the concentration of applied pesticide, in sediment (if available) and pore-water. Mean growth and percent survival of *Hyaella azteca* (10-d exposure) were the preferred metrics to evaluate whole-sediment toxicity. However, if these data were unavailable, substituted animal or plant toxicity metrics were applied. The number of chironomid genera and species richness were used to evaluate benthic community structure. We chose to rank chemistry, toxicity, and benthos using procedures developed by Kreis (1988) and used by Canfield et al. (1994). Accordingly, values for each individual variable for all stations (included reference) were scaled proportionally between 0 and 100 (e.g. 100 is the highest toxicity measured). The toxicity rank was determined by summing the ranks for both toxicity variables and re-ranking the results.

The criterion for evaluating chemistry was a concentration of pesticide or metal that exceeded either the risk quotient for sediment or the toxicity endpoint for an aquatic species in porewater (**Table 6**). The criterion for elevated toxicity was a significant

decrease in either of the toxicity variables used, relative to the control. The criterion for impacted benthos was either a Chironomidae genera richness or species richness value that was significantly different from the mean of the respective reference stations. A significant difference in benthos was tested using a two-sample t-test between each treated station and all reference stations.

Table 6. Threshold Values Applied in Chemistry Evaluation

Metal or Pesticide	Sediment Threshold	Sediment Threshold References	Pore-water Threshold	Porewater Threshold Reference
Copper Sulphate	LC50 (<i>Hyallolella azteca</i>) - 262 µg/g	Suedel <i>et al</i> 1996	LC50 (<i>H. azteca</i>) – 0.035 mg/l	Suedel <i>et al</i> 1996
Chelated Copper	LC50 (<i>Hyallolella azteca</i>) - 262 µg/g	Suedel <i>et al</i> 1996	LC50 (<i>H. azteca</i>) – 0.035 mg/l	Suedel <i>et al</i> 1996
Fluridone	N/A		EC50 (Stonewort) – 0.20 mg/l	Burkhart and Stross 1990
2,4-D	N/A		LC50 (<i>Chironomus plumosus</i>) – 100 mg/l	Washington, Dept. of Ecology 2001

Risk Quotient Calculation

Risk quotients were calculated according the method promulgated by the U.S. EPA (U.S. EPA, 1998). These risk quotients are part of the first step of a four part risk characterization process outlined in the ECOFRAM draft Aquatic Report (U.S. EPA, 1999). This report states,

“The purpose of the tiered process is to provide a logical progression of tests and risk assessment approaches to address the potential risks of toxicants to aquatic systems. The common feature of all tiered regulatory processes is a progression beginning with conservative assumptions and moving toward more realistic estimates. Tiered processes tend to be cost effective in that they ensure that resources are expended on pesticide product/issues meriting attention. ... The tiers are differentiated primarily by the data available at that state in the risk assessment process and the relative cost of achieving risk refinement appropriate for that tier of analysis.”

Risk quotients were calculated in order to identify where additional risk characterization work may be needed to fully explore potential impacts of aquatic pesticides. They only indicate where additional information may be needed and, in and of themselves, do not indicate impacts.

Aquatic Pesticide Monitoring Program
Final Report

In order to integrate water exposure information with water toxicity information, risk quotients (RQs) are calculated by dividing water chemical concentrations by an acute or chronic ecotoxicity value: $RQ = \frac{Exposure}{Toxicity}$ (U.S. EPA, 1998).

Exposure = an estimated environmental water concentration or actual water concentration field data.

Toxicity = an accepted toxicity measurement (i.e. LC50, LD50, EC50, EC25, NOEC, LOEC, or MATC).

The RQs calculated in this document used the highest pesticide concentration experimentally determined during our monitoring of the applications of a particular pesticide. The use of these peak values is appropriate for a Tier 1 risk characterization as such a characterization are meant to be protective, not predictive, and therefore based on conservative (i.e. worst-case) assumptions about potential exposure and effects. If possible risk is identified in a Tier 1 analysis, then a Tier 2 analysis (addressing the probability and magnitude of effects on sensitive species using conservative exposure scenarios) is indicated. Tier 2 analysis was not performed as part of this project.

The calculated RQs were then compared to a Level of Concern (LOC) determined by the U.S. EPA Office of Pesticide Programs (OPP). The specific LOCs for aquatic animals and plants are shown in **Table 7**. LOCs are unit-less values that allow for simple determination of possible exceedances of regulatory limits. An LOC exceedance is indicative only of the need for further investigation of an application scenario.

Table 7. Aquatic Animal and Plant Levels of Concern

Risk Presumption	RQ	LOC
Acute Risk	EC/LC50 or EC50	0.5
Acute Restricted Use	EC/LC50 or EC50	0.1
Acute Endangered Species	EC/LC50 or EC50	0.05
Chronic Risk	EC/ MATC or NOEC	1

The U.S.EPA interprets exceedances of LOCs as follows:

Acute high risk: potential for acute risk is high; regulatory action may be warranted in addition to restricted use classification

Acute restricted use: the potential for acute risk is high, but this may be mitigated through restricted use classification

Acute endangered species: the potential for acute risk to endangered species is high, but this may be mitigated through restricted use classification

Chronic risk: the potential for chronic risk is high; regulatory action may be warranted

Values for standard toxicity test species were used, as were values for any listed species present. Where there are multiple toxicity values for the same test species, the lowest value was selected. The toxicity measurements used were from peer-reviewed academic literature, FIFRA registration documents, or other government reports.

Risk quotients were also calculated for sediment pesticide concentrations where toxicity values were available. However, the U.S. EPA LOCs were not applicable to sediment pesticide concentrations and there were no comparable regulatory values for sediment.

Results

2,4-D

U.S. Fish and Wildlife Service employees applied the herbicide Weedar 64 (2,4-D dimethylamine salt) mixed with R-11 surfactant (a nonylphenoethoxylate surfactant) to a main stem slough of South Stone Lake within the Stone Lake National Wildlife Refuge (SLNWR) on September 8, 2003. 2,4-D (DMA) and 2,4-D (BEE) are both registered for aquatic use, but have different toxicological properties making it important to differentiate between the compounds when reviewing data. Portions of South Stone Lake are repeatedly treated with 2,4-D and surfactant during the summer and early fall to control heavy infestations of water hyacinth (*Eichornia crassipes*). Different sections of this lake are treated with glyphosate for hyacinth control. The 2,4-D is applied to the emergent vegetation via an automated spray nozzle water pump system mounted on an airboat. The study area was approximately 0.15 acres, densely covered by hyacinth, with a sand/silt-consolidated substrate. The application rate at the site was 30 liquid ounces of herbicide per 50 gallons water. The nonylphenol surfactant was added to the pesticide tank mix.

Tables 10 and 11 summarize the sediment quality triad measurements for the 2,4-D application at SLNWR. This data indicates that there is no evidence of pesticide induced degradation at either of the sampling locations. In addition, no LOCs were exceeded by the maximum 2,4-D concentration measured (**Table 8**).

However, the R-11 surfactant concentration was four times the acute endangered species LOC for Delta smelt (**Table 9**). Seeing an LOC exceedance for R-11 (a nonylphenol containing surfactant) is not unexpected given that the R-11 LC50 for Delta smelt is an order of magnitude lower than the 2,4-D Delta smelt LC50.

Table 8. Peak Concentration Risk Quotient Calculations for 2,4-D Application

Experimental Concentration Range	Toxicity Value	Toxicity measurement, regulatory tolerance, action or guidance value	Risk Quotient	RQ exceeds LOC or other regulatory guideline?
27.5 µg/l	315 µg/l	Chinook salmon LC50	0.087	No
	7.2 mg/l	<i>D. magna</i> LC50	0.0038	No
	100 mg/l	<i>P. promelas</i> LC50	0.000275	No
	128 mg/l	Delta smelt NOEC	0.000215	No

Table 9. Peak Concentration Risk Quotient Calculations for Surfactant (R-11) during 2,4-D Application.

Experimental Concentration Range	Toxicity Value	Toxicity measurement, regulatory tolerance, action or guidance value	Risk Quotient	RQ exceeds LOC or other regulatory guideline?
22.6 µg/l	5700 µg/l	<i>C. dubia</i> LC50	0.004	No
	420 µg/l	<i>C. dubia</i> NOEC	0.05	No
	1100 µg/l	<i>P. promelas</i> LC50	0.02	No
	340 µg/l	<i>P. promelas</i> NOEC	0.06	No
	700 µg/l	Delta smelt LC50	0.03	No
	100 µg/l	Delta smelt NOEC	0.2	Yes (Acute Endangered)
	3900 µg/l	Sacramento splittail LC50	0.006	No
	1900 µg/l	Sacramento splittail NOEC	0.01	No

APMP research has indicated that 2,4-D alone and in combination with a nonylphenol surfactant may cause endocrine disruption in juvenile *O. mykiss* at label-approved application rates. Work is continuing to determine if 2,4-D itself is an endocrine disruptor or if dichlorophenol (a primary 2,4-D breakdown product) is the source of the vitellogenin induction.

Aquatic Pesticide Monitoring Program
Final Report

Table 10. Sediment Quality Trend Calculations for 2, 4-D (DMA)

Site	Station	2,4-D		Amphipod		Amphipod %		Toxicity Rank	Number of Chironomidae		Species Richness	
		porewater	rank	Mean Length	rank	Survival	rank		Genera	rank	Richness	rank
Stone Lake	SL2-01	0.49	96	0.39	0	96.25	0	0	6.00	50	9.67	75
Stone Lake	SL2-02	0.00	0	0.25	100	96.25	0	54	2.00	0	8.67	100
Pre-App		0.51	100	0.27	85	88.75	100	100	10.00	100	12.67	0

Data are an average of individual replicates at pre-app (reference) vs. 2wk (each treated station)

Chemistry, toxicity, and benthos are scaled proportionally between 0 (e.g. low toxicity) and 100 (e.g. high toxicity)

Toxicity and Benthos (species richness only) are reverse ranked to reflect assumed relationship to metal application

The toxicity rank is the combined ranking of both mean length and percent survival ranks for *Hyaella azteca*

Table 11. Summary of 2, 4-D (DMA) Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	Stone Lake (2,4-D) 2003	Possible Conclusion
+	+	+		Evidence of pesticide-induced degradation
-	-	-	SL201, SL202	No evidence of pesticide induced degradation
+	-	-		Pesticides are not bioavailable
-	+	-		Chemicals other than pesticide or conditions exist with potential to cause degradation
-	-	+		Benthic response not due to pesticide
+	+	-		Pesticide may be stressing the system
-	+	+		Chemicals other than pesticide or conditions are causing degradation
+	-	+		Pesticide is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a metal concentration that exceeded either the porewater LC50 reported for *Chironomus plumosus*

A plus(+) for toxicity indicates a significant decrease relative to control in either amphipod growth or percent survival

A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the reference stations

Copper Sulfate

Copper sulfate was monitored in all three years of the project at four reservoirs in Marin Municipal Water District (MMWD). Copper sulfate is applied to the Marin reservoirs for floating and benthic algae control.

Two reservoirs received copper treatments (Nicasio and Bon Tempe Reservoirs) and two untreated reservoirs were used at reference locations (Soulajule Reservoir and Lake Lagunitas). Soulajule Reservoir was only sampled during year one. Nicasio and Soulajule reservoirs are located in the West Marin watershed. Lake Lagunitas and Bon Tempe reservoir are located in the Mount Tamalpais watershed. Nicasio Reservoir was treated for floating algae with copper sulfate applied by dissolution of granular copper sulfate through burlap bags towed with a boat. Bon Tempe Reservoir was treated with granulated copper sulfate for benthic algae control. Granulated copper was applied with a hopper, mounted to the side of a boat. Soulajule Reservoir has never been treated with copper and Lake Lagunitas has not been treated since the 1920s.

Tables 13 and 14 summarize the sediment quality triad measurements for the copper sulphate applications in the MMWD. This analysis indicates that multiple stations in Bon Tempe reservoir showed evidence of copper induced degradation. The impacted locations vary between years of data collected mostly likely due to the variation of sediments within the samples areas. In Nicasio reservoir, no sites exhibited degradation of all three lines of data, but three sites did show the potential for ecosystem impacts.

Experimental concentrations and risk quotients are summarized in **Tables 12**.

Table 12. Water Risk Quotient Calculations for Copper Sulfate Applications (Reservoir System)

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		Peak Concentration	t+24 hour conc.	t+1 week conc.
		0.0653 mg/l	0.0381 mg/l	0.0076 mg/l
0.068 mg/l	<i>C. dubia</i> EC50	<u>0.96</u>	<u>0.56</u>	<u>0.11</u>
0.03 mg/l	Daphnid NOEC	<u>2.18</u>	<u>1.27</u>	0.25
0.8 mg/l	Rainbow Trout 48hr LC50	0.08	0.048	0.0095
2300 mg/l	Duckweed EC50	.00003	1.6E-5	3.3E-6

Aquatic Pesticide Monitoring Program
Final Report

Water toxicity testing in Bon Tempe found acute water toxicity to *O. mykiss* and acute and chronic toxicity to *C. dubia* shortly after copper application. Water toxicity was found at all time intervals after application. Inhibition of *C. dubia* reproduction was the primary toxicity measure detected, but the magnitude of toxicity did not always reflect the measured copper concentrations in the water. The most significant reproductive and mortality effects took place immediately after application. Significant trout mortality occurred in one sample collected immediately after application. The 24 hour and one week post-application samples also inhibited reproduction of *C. dubia* although concentrations did not exceed the copper LOEC for inhibition.

Aquatic Pesticide Monitoring Program
Final Report

Table 13. Sediment Quality Trend Calculations for Copper Sulphate

Site	Station	Copper Sed	rank	Copper porewater	rank	Amphipod Mean Length	rank	Amphipod % Survival	rank	Toxicity Rank	Number of Chironomidae Genera	rank	Species Richness	rank
Bon Tempe	B-01	2390.00	89	0.05	100	0.08	73	68.00	100	100	4.08	33	7.33	80
Bon Tempe	B-02	733.67	26	0.04	79	0.13	27	99.00	0	1	2.00	0	4.17	100
Bon Tempe	B-03	2693.33	100	0.05	98	0.07	89	82.50	53	79	2.83	13	5.42	92
Bon Tempe	B-04	687.00	24	0.01	25	0.06	100	85.00	45	81	4.33	37	7.42	79
Bon Tempe	B-05	935.67	34	0.02	33	0.10	58	91.00	26	39	3.42	22	5.92	89
Bon Tempe	B-06	474.00	16	0.01	10	0.14	10	94.00	16	0	4.83	45	12.17	49
Lagunitas	L-01	46.43	0	0.00	0	0.13	27	90.00	29	21	8.33	100	19.75	0
Lagunitas	L-02	56.13	0	0.00	2	0.11	45	92.00	23	28	4.83	45	11.92	50
Lagunitas	L-03	46.50	0	0.00	0	0.15	0	82.00	55	20	7.50	87	16.58	20
Bon Tempe	B-01	682.00	55	0.00	0	0.17	97	95.33	6	52	6.33	0	8.89	79
Bon Tempe	B-02	1200.00	100	0.03	55	0.17	100	81.60	100	100	7.33	37	7.22	100
Bon Tempe	B-03	437.00	34	0.01	3	0.21	79	94.50	12	45	8.67	88	9.22	75
Bon Tempe	B-04	449.67	35	0.00	0	0.17	96	85.00	77	86	6.67	13	7.89	92
Bon Tempe	B-05	338.50	26	0.02	53	0.19	88	87.00	63	76	7.33	37	10.22	63
Bon Tempe	B-06	388.50	30	0.00	0	0.22	75	95.50	5	40	8.00	63	10.78	56
Lagunitas	L-01	40.60	0	0.04	100	0.37	0	96.25	0	0	9.00	100	15.33	0
Nicasio	N-05	99.65	100	0.00	34	0.18	81	74.00	100	100	6.00	0	6.50	86
Nicasio	N-06	38.75	15	0.00	19	0.22	10	93.50	19	0	6.50	20	9.17	14
Nicasio	N-07	28.05	0	0.01	100	0.23	0	81.50	69	26	8.50	100	9.50	5
Nicasio	N-14	56.60	40	0.00	21	0.16	100	90.00	33	69	8.00	80	9.67	0
Nicasio Ref	N-11	59.2	44	0.00	0	0.21	29	98.00	0	0	7.00	40	7.00	73
Nicasio Ref	N-13	52.90	35	0.00	10	0.19	55	90.00	33	39	6.00	0	6.00	100

Data are an average of individual replicates at each application time.

Chemistry, toxicity, and benthos are scaled proportionally between 0 (e.g. low toxicity) and 100 (e.g. high toxicity).

Toxicity and Species richness are reverse ranked to reflect assumed relationship to toxicity.

The toxicity rank is the combined ranking of both mean length and percent survival ranks for *Hyaella azteca*.

Aquatic Pesticide Monitoring Program
Final Report

Table 14. Summary of Copper Sulphate Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	2003 Stations	2004 Stations	Possible Conclusion
+	+	+	B01, B02, B04	B01, B02, B03, B04, B05	Evidence of copper-induced degradation
-	-	-		N07, N06, N14	No evidence of copper induced degradation
+	-	-	B06		Copper is not bioavailable
-	+	-		N05	Chemicals other than copper or conditions exist with potential to cause degradation
-	-	+			Benthic response not due to copper
+	+	-	B05		Metals may be stressing the system
-	+	+			Chemicals other than copper or conditions are causing degradation
+	-	+	B03	B06	Copper is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a concentration of Cu that exceeded either the Sediment Quality Guideline ERL for Cu or porewater reported in Suedel et al. 1996.

A plus(+) for toxicity indicates a significant decrease relative to control in either amphipod growth or percent survival.

A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the Lagunitas reference stations.

Chelated Copper

Chelated copper was monitored within the canal systems of Solano Irrigation District (SID) and Potter Valley Irrigation District (PVID). The chelated copper is applied to the ID canals for macrophyte and filamentous algae control. SID applied Clearigate® which is a copper ethanalamine mixture in an emulsified formulation. PVID applied Cutrine Plus® which is a copper ethanalamine mixture. Both products contain unique unspecified ‘inert ingredients’ that may cause them to have different environmental fates and toxicological properties. In the two irrigation district system canals monitored, the copper treatments consisted of chelated copper pumped into the canals as the water passed through a weir to aid in mixing. Each treatment lasted for a 2-3 hours.

Tables 16 and 17 summarize the sediment quality triad measurements for the chelated copper applications in Byrnes Canal. These measurements indicate that copper induced degradation occurs at one site and may be stressing the system at the other site.

Water toxicity testing in conjunction with these applications showed intermittent toxicity before and after application. The peak water concentrations detected during the three applications exceed the LOCs. Experimental concentrations and risk quotients are summarized in **Table 15**.

Table 15. Water Risk Quotient Calculations for Chelated Copper Applications (Irrigation Canal Systems)

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		Peak Concentration	t+4 hour conc.	t+11 hour conc
		1.43 mg/l	0.0988 mg/l	0.0988 mg/l
9.9 mg/l	Water flea <i>Alonella</i> LC50	<u>0.144</u>	0.01	0.002
0.0023mg/l	Fathead Minnow larvae 48hr LC50	<u>621</u>	<u>43</u>	<u>7.39</u>

Aquatic Pesticide Monitoring Program
Final Report

Table 16. Sediment Quality Trend Calculations for Chelated Copper

Site	Station	Copper Sed	Copper rank	Copper porewater	Copper rank	Amphipod Mean Length	Amphipod rank	Amphipod % Survival	Amphipod rank	Toxicity Rank	Number of Chironomidae Genera	rank	Species Richness	rank
Byrnes Canal	BC-01	609.00	100	0.01	0	0.17	68	58.00	32	50	18.00	100	28.67	0
Byrnes Canal	BC-02	211.00	0	0.01	1	0.16	100	35.00	100	100	8.00	0	19.67	52
Pre-App		565.50	89	0.13	100	0.20	0	69.00	0	0	11.00	30	11.33	100

Data are an average of individual replicates at pre-app (reference all stations) vs. 2wk (per treated station)
Chemistry, toxicity, and benthos are scaled proportionally between 0 (e.g. low toxicity) and 100 (e.g. high toxicity)
Toxicity and Benthos (species richness only) are reverse ranked to reflect assumed relationship to metal application
The toxicity rank is the combined ranking of both mean length and percent survival ranks for *Hyalella azteca*

Table 17. Summary of Chelated Copper Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	Byrnes Canal 2003	Possible Conclusion
+	+	+	BC01	Evidence of copper-induced degradation
-	-	-		No evidence of copper induced degradation
+	-	-		Copper is not bioavailable
-	+	-	BC02	Chemicals other than copper or conditions exist with potential to cause degradation
-	-	+		Benthic response not due to copper
+	+	-		Metals may be stressing the system
-	+	+		Chemicals other than copper or conditions are causing degradation
+	-	+		Copper is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a metal concentration that exceeded either the Sediment Quality Guideline ERL or porewater LC50 reported for *Hyalella azteca*
A plus(+) for toxicity indicates a significant decrease relative to control in either amphipod growth or percent survival
A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the reference stations

Diquat Dibromide

Diquat dibromide was sampled at two locations during the APMP. One location was at a homeowners association property where diquat was applied to treat sago pondweed by a local licensed pesticide applicator. The second location was in 7-Mile Slough in the Sacramento/ San Joaquin Delta where diquat was applied by Department of Boating and Waterways staff for control of *Egeria densa*.

Water chemical characterization and toxicity testing were conducted during both sampling events. Limited sediment monitoring was conducted because diquat adsorbs irreversibly to sediment and once bound is no longer considered bioavailable.

At the Sand Bay site, diquat was found at 300 and 400 ppb immediately after application. This concentration was double that of the highest concentration found at 7-Mile Slough (195 ppb). Peak water diquat dibromide concentration risk quotients exceeded LOCs at both applications. Interestingly, LOC exceedances were observed before application at the Delta site. This is indicative of diquat runoff from upstream urban and terrestrial applications. Experimental concentrations and risk quotients are summarized for diquat in **Table 18**.

Aquatic Pesticide Monitoring Program
Final Report

Table 18. Water Risk Quotient Calculations for Diquat Dibromide Applications

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		preapplication conc.	t+1 hour conc.	t+24 hours conc.
		7-Mile: 13.8 µg/l Sand Bay: 0.79 µg/l	7-Mile: 180 µg/l Sand Bay: 400 µg/l	7-Mile: 4.5 µg/l
19 µg/l	<i>S. capricornutum</i> . EC50 (growth)	<u>RQ_{7-Mile}=0.73</u> RQ _{Sand Bay} =0.04	<u>RQ_{7-Mile}=9</u> <u>RQ_{Sand Bay}=21</u>	<u>RQ_{7-Mile}=0.24</u>
44 µg/l	Algae NOEC (biomass growth)	RQ _{7-Mile} =0.31 RQ _{Sand Bay} =0.02	<u>RQ_{7-Mile}=4</u> <u>RQ_{Sand Bay}=9</u>	RQ _{7-Mile} =0.1
32 µg/l	<i>D. magna</i> LC50	<u>RQ_{7-Mile}=0.43</u> RQ _{Sand Bay} =0.025	<u>RQ_{7-Mile}=5.6</u> <u>RQ_{Sand Bay}=13</u>	<u>RQ_{7-Mile}=0.14</u>
36 µg/l	Daphnid NOEC	RQ _{7-Mile} =0.38 RQ _{Sand Bay} =0.02	<u>RQ_{7-Mile}=5</u> <u>RQ_{Sand Bay}=11</u>	RQ _{7-Mile} =0.125
120 µg/l	Minnow NOEC	RQ _{7-Mile} =0.115 RQ _{Sand Bay} =6E-3	<u>RQ_{7-Mile}=1.5</u> <u>RQ_{Sand Bay}=3.3</u>	RQ _{7-Mile} =0.038
7600 µg/l	<i>P. promelas</i> LC50	RQ _{7-Mile} =0.0018 RQ _{Sand Bay} =1E-4	RQ _{7-Mile} =0.02 RQ _{Sand Bay} =0.05	RQ _{7-Mile} =6E-4
11 µg/l	Duckweed LOEC	<u>RQ_{7-Mile}=1.25</u> RQ _{Sand Bay} =0.72	<u>RQ_{7-Mile}=16</u> <u>RQ_{Sand Bay}=36</u>	RQ _{7-Mile} =0.4
18 µg/l	Duckweed EC50	<u>RQ_{7-Mile}=0.76</u> RQ _{Sand Bay} =0.044	<u>RQ_{7-Mile}=10</u> <u>RQ_{Sand Bay}=22</u>	<u>RQ_{7-Mile}=0.25</u>

Fluridone

Fluridone (in the form of Sonar®) was monitored at multiple locations during the three years of the APMP. In 2002, a liquid fluridone application was monitored in Merced Irrigation District's Main Canal and pelleted applications in Clear Lake. In 2003 monitored consisted of pelleted fluridone applications to Big Bear Lake (San Bernardino mountains) and liquid fluridone applications to Costa Ponds (a fishing resort near Porterville California). In 2004, more extensive sediment analysis of Clear Lake was conducted to investigate long term non-target plant toxicity. Only at the Big Bear Lake and Costa Pond applications were sufficient data collected to performed sediment quality triad analysis. Typha seed germination and plant growth toxicity test was used for samples collected from Big Bear Lake, Clear Lake, and Costa Ponds. In addition to seed germination rate, both the mean root and shoot growth were recorded as sublethal endpoints.

Tables 20 and **21** summarize the sediment quality triad measurements for the fluridone applications to Big Bear Lake and Costa Ponds. These measurements indicate that fluridone induced degradation occurred at three Costa Ponds sites and one Big Bear Lake Site. At other sites, some lines of evidence indicate ecosystems impacts.

In 2004, multiple Clear Lake sediment and porewater samples were collected to investigate the potential long term toxicity to non-target plant organisms. Clear Lake shore segments have been treated at different intervals over the preceding decade. Samples were collected from sites that had not been treated for a varying number of years. However, site conditions make it likely that fluridone containing sediment is constantly transported through the lake making toxicity test results inconclusive.

Tissue samples (Sacramento suckers, crayfish, and rainbow trout) were collected during the Merced Irrigation District (MID) eight week application of liquid fluridone in their Main Canal. The data indicate that fluridone accumulated in tissue during the applications and persisted two weeks following application. At four weeks after the cessation of treatment, tissue concentrations had returned to pre-application levels. No LOC exceedances were observed with the MID applications (**Table 19**).

Aquatic Pesticide Monitoring Program
Final Report

Table 19. Peak Risk Quotient Calculations for Fluridone Application at MID Main Canal

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		Pre-application concentration	Mid Application	Post-application
		Non Detect	37 µg/l	102 µg/l
2.1 mg/l	<i>D. magna</i> LC50	0	0.018	0.048
200 µg/l	<i>D. magna</i> NOEC	0	0.185	0.51
6.2 mg/l	<i>P. promelas</i> LC50	0	0.006	0.016
1.88 mg/l	<i>P. promelas</i> NOEC	0	0.02	0.054
1.28 mg/l	Delta smelt NOEC	0	0.029	0.08

Aquatic Pesticide Monitoring Program
Final Report

Table 20 Sediment Quality Trend Calculations for Fluridone

Site	Station	Fluridone Pore Water	rank	Typha Mean Root Length	rank	Typha % Germination	rank	Toxicity Rank	Number of Chironomidae Genera	rank	Species Richness	rank
Costa Ponds	CP-02	0.92	80	10.40	37	96.65	67	27	3.00	100	5.78	35
Costa Ponds	CP-03	1.16	100	9.20	100	98.90	0	21	2.67	67	7.00	0
Costa Ponds	CP-04	0.84	73	11.10	0	95.55	100	21	2.33	33	5.78	35
Costa Ponds	CP-05	1.03	89	10.15	50	95.55	100	100	2.00	0	6.33	19
Costa Ponds Ref	CP-01	0.00	0	9.45	87	98.90	0	0	2.33	33	3.56	100
Big Bear	BBP-01	0.18	9	8.40	100	100.00	0	100	7.00	67	11.00	48
Big Bear	BBP-02	0.28	17	8.70	90	100.00	0	88	4.00	17	5.67	100
Big Bear	BBP-03	0.08	0	9.70	55	100.00	0	46	5.00	33	8.00	77
Big Bear	BBE-01	0.99	78	10.80	17	100.00	0	0	4.00	17	9.00	68
Big Bear	BBE-02	1.24	100	11.30	0	97.80	100	100	3.00	0	12.00	39
Big Bear Ref	BBC-01	0.17	8	9.30	69	100.00	0	63	9.00	100	16.00	0

Data are an average of individual replicates at each application time

Chemistry, toxicity, and benthos are scaled proportionally between 0 (e.g. low toxicity) and 100 (e.g. high toxicity)

Toxicity and Benthos (species richness) are reverse ranked to reflect assumed relationship to toxicity

The toxicity rank is the combined ranking of both mean root length and percent germination for Typha latifolia

Table 21 Summary of Fluridone Sediment Quality Trend Data

Chemistry	Toxicity	Benthos	Stations	Possible Conclusion
+	+	+	BBP02, CP02, CP03, CP05	Evidence of pesticide-induced degradation
-	-	-		No evidence of pesticide induced degradation
+	-	-	BBE01, BBE02	Pesticides are not bioavailable
-	+	-	BBP01, BBP03	Chemicals other than pesticide or conditions exist with potential to cause degradation
-	-	+		Benthic response not due to pesticide
+	+	-		Pesticide may be stressing the system
-	+	+		Chemicals other than pesticide or conditions are causing degradation
+	-	+	CP04	Pesticide is not bioavailable or benthic response is not due to chemistry

A plus(+) for chemistry indicates a metal concentration that exceeded the porewater EC50 reported for Stonewort

A plus(+) for toxicity indicates a significant decrease relative to control in either plant growth or percent germination

A plus(+) for benthos indicates either a chironomid genera richness or total species richness value that was significantly different from the reference stations

Glyphosate

Glyphosate was monitored at four locations during the APMP. There were three canal sites; 1) Doris Drain, an agriculture return flow canal, near Ventura, 2) Merced Irrigation District's Atwater Canal, and 3) an Orange County Public Works Department stormwater canal. Glyphosate applications were also monitored at Stone Lake National Wildlife Refuge. All applications were made with a tank mix of glyphosate and nonionic nonylphenoethoxylate surfactant. Triad monitoring was conducted only at SLNWR.

Since glyphosate is considered to be biologically unavailable once it is sediment bound, only limited sediment quality data was gathered and sediment quality triad calculations were not performed. At all sampling sites, no acute or acute-restricted LOC exceedances occurred. All the sites where glyphosate was applied were lotic systems where chronic exposures could not have occurred.

The Doris Drain application showed the highest glyphosate water concentrations (up to 1800 ppb immediately after treatment). No LOC exceedances for nontarget organisms were observed. However several exceedances were observed for the R-11 surfactant applied in conjunction with the glyphosate (**Table 22**).

Table 22. Risk Quotient Calculations for Surfactant (R-11) during Glyphosate Application at Doris Drain.

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)		
		preapplication conc.	t+0 hour conc.	t+3 hour conc.
		<RL µg/l	120 µg/l	19.6 µg/l
5700 µg/l	<i>C. dubia</i> LC50	0	0.021	0.003
420 µg/l	<i>C. dubia</i> NOEC	0	0.29	0.047
1100 µg/l	<i>P. promelas</i> LC50	0	<u>0.11</u>	0.018
340 µg/l	<i>P. promelas</i> NOEC	0	0.35	0.058
700 µg/l	Delta smelt LC50	0	<u>0.17</u>	0.028
100 µg/l	Delta smelt NOEC	0	<u>1.2</u>	0.196
3900 µg/l	Sacramento splittail LC50	0	0.031	0.005
1900 µg/l	Sacramento splittail NOEC	0	0.063	0.01

Methoprene

Methoprene was monitored in conjunction with an application made to a tidally influenced wetland (Swanton's Marsh) near the town of Martinez. The wetland is situated between the Tesoro Corporation refinery and the Concord Naval Weapons station. The wetland is fed from inland streams that also flow through methoprene treated marshes upstream. Normally Swanton's marsh is treated with a mixture of methoprene and *Bacillus thuringiensis israelensis*, but for the benefit of this research the Contra Costa Mosquito Vector control district modified their application routine and only methoprene was applied.

This is the only site where an insecticide was monitored during the APMP. Therefore, the methods used at this site differ significantly from those at the herbicide monitoring locations. At this site, water, porewater, and sediment chemical characterization, laboratory sediment toxicity testing, and *in-situ* sediment toxicity testing were performed. The laboratory toxicity test used larval insect *Chironomus tentans* in 10-day survival and growth tests. The *C. tentans* are more sensitive to methoprene than *H. azteca*.

In addition, *in-situ* *H. azteca* toxicity tests were performed. The literature review and conversations with mosquito vector control scientists indicated that methoprene has a short window of bioavailability after application. To attempt to conduct a test within the methoprene breakdown time frame, *in-situ* exposures were attempted. The test method was modified from the EPA standard *H. azteca* test methodology by UC Davis Marine Pollution Studies Laboratory scientists.

Methoprene was not detected in any water samples collected from the site. Methoprene is known to degrade quickly in water and sunlight. The day sampling occurred when no clouds were present and the temperature was over 100°F.

Aquatic Pesticide Monitoring Program
Final Report

Methoprene was detected in all sediment porewater samples (including before application and reference site). The concentrations ranged from 11.6-22.6 ppb. Methoprene was found in the sediments at concentrations ranging from 178-2080 ppb. At the reference site, the methoprene concentration was 178 ppb before application and 1800 ppb 4 days after application. The reference site is highly influenced by tidal flow and receives sediment from upstream locations. These upstream locations are treated with methoprene, but are not immediately adjacent to the reference site. Peak water methoprene concentration risk quotients did not exceed LOCs. Experimental concentrations and risk quotients are summarized in **Table 23**.

Swanton’s marsh is treated with methoprene approximately twice a month. The fact that methoprene was found before application indicates that it is persistent in the soil for several weeks. U.S. EPA methoprene registration documents state that methoprene is persistent in the soil for up to 10 days, is tightly bound to soil, and is degraded primarily by microbes (U.S. EPA, 1982).

Table 23. Peak Concentration Risk Quotient Calculations for Methoprene Application

Experimental Concentration Range	Toxicity Value	Toxicity measurement, regulatory tolerance, action or guidance value	Risk Quotient	RQ exceeds LOC or other regulatory guideline?
Porewater				
22.6 µg/l	2 µg/l	<i>M. bahia</i> LOEC	11.3	Yes
	1250 µg/l	<i>H. azteca</i> LC50	0.018	No

The *C. tentans* toxicity tests were inconclusive. Significant mortality was seen at the two treated sites before and after application. Significant reduction in growth was seen in the samples collected at all three sites before and after application. Many of the sediments from this site were highly anoxic. It is likely that the anaerobic nature of the sediments were the cause of the significant growth reductions and observed mortality. Dissolved oxygen concentrations at the three sites averaged 3.6 mg/l. Total ammonia concentrations ranged from 11.6-4.0 mg/l (average 8.54 mg/l). Total sulfide ranged from 0.21-<0.01 (average 0.1 mg/l).

The in-situ *H. azteca* tests were also inconclusive. *H. azteca* were healthy at 96 hours, but the majority of test organisms were dead after 10 days. The test animals may have died due to environmental conditions (anoxia) or lack of food in the 10-day exposures.

The inconclusive results of the two types of toxicity tests at this site highlight the difficulty of conducting monitoring at such a site. Methoprene is applied to control larval mosquitoes. The preferred habitat for the mosquito larvae are very shallow still waters, conditions that often lead to anaerobic conditions.

Triclopyr

California Department of Food and Agriculture (CDFA) personnel applied Renovate® triclopyr triethylamine salt at Bear Creek in 2003. A one percent triclopyr and 0.5 percent Target Prospread Activator (TPA), a surfactant, by volume solution was applied to an approximately 0.34 acre creek section for the control of dense native water primrose (*Ludwigia sp.*). The herbicide tank mix was applied with a backpack hand-pump sprayer to the surface of the floating vegetation mats. As triclopyr had only recently received its aquatic use label, the number of applications made during the APMP was very limited.

Although triclopyr is likely to partition to sediment, sediment was not collected at this site because the creek bed was predominantly cobbles covered by a fine layer of silt. The cobbles made it impossible to collect enough sediment for analysis with a sediment sampler. The layer of silt present was too thin to gather enough sediment for analysis by any other means. This lack of sediment data made it impossible to conduct sediment quality triad analysis of the application.

Water chemistry results indicated that there were no triclopyr risk quotient LOC exceedances. Water toxicity tests were inconclusive due to sampling error.

Nonylphenoethoxylate surfactant was found in the creek water both before and after application (**Table 24**). Upstream sources could not be identified. The post-application samples showed continuous increases in concentration with the maximum value at 24 hours after application (2390 ppb). This peak could be due to additional upstream inputs or a dispersion pattern different from that of triclopyr. The surfactant risk quotients show LOC exceedances before and after application for a variety of aquatic animal species.

Table 24. Risk Quotient Calculations for Surfactant during Triclopyr Application.

Toxicity Value	Toxicity measurement or guidance value	Risk Quotients (Risk quotients in bold and underlined indicate an LOC exceedance)			
		preapplication conc.	t+0 hour conc.	t+2 hours conc.	t+24 hours conc.
		570 µg/l	Non Detect	185 µg/l	2390 µg/l
5700 µg/l	<i>C. dubia</i> LC50	<u>0.1</u>	0	0.032	<u>0.42</u>
420 µg/l	<i>C. dubia</i> NOEC	<u>1.36</u>	0	0.44	<u>5.7</u>
1100 µg/l	<i>P. promelas</i> LC50	<u>0.52</u>	0	<u>0.17</u>	<u>2.17</u>
340 µg/l	<i>P. promelas</i> NOEC	<u>1.68</u>	0	0.54	<u>7.03</u>
700 µg/l	Delta smelt LC50 ^a	<u>0.81</u>	0	<u>0.26</u>	<u>3.41</u>
100 µg/l	Delta smelt NOEC ^a	<u>5.7</u>	0	<u>1.85</u>	<u>23.9</u>
3900 µg/l	Sacramento splittail LC50 ^a	<u>0.15</u>	0	0.047	<u>0.61</u>
1900 µg/l	Sacramento splittail NOEC ^a	0.30	0	0.097	<u>1.26</u>

^a. Delta smelt and Sacramento splittail toxicity data for R-11. TPA and R-11 have very similar chemical and toxicity characteristics.

CONCLUSIONS

Use of the data gathered during the three pesticide application seasons of the APMP should be limited to screening purposes only, to identify where further risk characterization or research may be needed. The APMP generated chemical characterization, toxicity, and bioassessment data. The chemical characterization and toxicity data generated can be used for screening purposes. In complex field situations, bioassessments require multiple years of data before even preliminary conclusions can be drawn.

Specific conclusion concerning individual pesticides:

2,4-D

Only one application of 2,4-D (in the 2,4-D dimethylamine salt formulation) with added surfactant was monitored. At this single application, no toxicity was observed nor did risk quotients indicate the need for further information. Vitellogenin induction laboratory experiments indicated that 2,4-D may cause endocrine disruption at legal application rates.

The vitellogenin induction studies indicated the need for further study of the aquatic 2,4-D formulations and their primary breakdown products. This level of research should not be expected from entities conducting compliance monitoring.

Acrolein

Due to acrolein's rapid volatilization, work focused on development of a field sampling method that would allow for accurate determination of the pesticide in water. Current standard environmental sampling methods are inadequate for sampling of acrolein treated water and result in suspect results.

Refinement of the sampling methodology began in 2003. Results indicated that the method developed was successful at low acrolein water concentrations. This refined method enables the determination of acrolein residue values.

Due to acrolein's rapid volatilization, it is currently not possible to conduct standard water toxicity tests. Since acrolein exhibited extremely low Lowest Observable Effect Concentration (LOEC) values, the detectable presence of acrolein indicated that very high mortality to EPA water and sediment toxicity test species can be assumed.

The development of diagnostic response tests (i.e. phytomonitoring, sentinel bivalves and fish, etc.) were explored and additional work is warranted. These tests have the potential to provide a low cost, low tech method of detecting acrolein outside of designated treatment areas.

Copper Sulfate

Copper sulfate applications were monitored in three reservoirs. In one reservoir treatment area dissolved copper sulfate toxicity was observed in juvenile trout and Ceriodaphnia immediately after and up to a week following application. Peak concentration risk quotients showed acute and chronic U.S. EPA Office Pesticide Programs Levels-of-Concern (LOC) exceedances. At 24 hours after application the risk quotients showed acute and chronic LOC exceedances. At one week after application the risk quotients showed acute LOC exceedances.

In the reservoir treated with granular copper sulfate applications, significant mortality was observed in Ceriodaphnia and juvenile trout water toxicity tests

immediately after application within the treated area. Mortality and growth inhibition was also observed in a number of the sediment samples. Sediment copper concentrations at many sites exceeded a published *Hyallela azteca* LC50 value. However, the toxicity observed in the sediments indicated that the majority of the copper was not bioavailable.

These findings indicate the need for further risk characterization associated with copper sulfate applications.

Chelated Copper

Chelated copper pesticides were monitored during applications in two irrigation canal systems. One system used a product of mixed copper ethanolamines and the other the same product of mixed copper ethanolamines in an emulsified formulation. Chelated copper formulations are likely to have distinct behavior between copper sulfate and each other in aquatic environments based on the chelating agent and other adjuvants. It should be noted that copper carbonate is the active ingredient in other chelated copper products and no monitoring of copper carbonate based pesticides was conducted.

In both monitored systems, the water samples were similarly toxic before and after application. Therefore, no definitive conclusions can be drawn about the toxicity of mixed copper ethanolamines. The sediment quality triad calculations indicated the possibility of copper impacts to the system.

Further risk characterization associated with chelated copper applications is warranted.

Glyphosate

Glyphosate was monitored at several locations. No toxicity was found to be associated with glyphosate applications. Glyphosate is often applied with a surfactant which may have much higher toxicity than the active ingredient.

Based on risk quotient calculations and toxicity data, no further risk characterization associated with glyphosate applications alone is warranted. Risk characterizations are warranted when a surfactant used in conjunction with the glyphosate.

Diquat Dibromide

Diquat dibromide was sampled at two locations, one small pond and a delta slough. Diquat risk quotients similarly exceeded Levels-of-Concern at all sampling periods in the Delta slough (including pre-application) and at one hour after application in the pond. Diquat may be applied with a surfactant which may have much higher toxicity than the active ingredient. Diquat sediment concentrations were not considered, as diquat is irreversibly adsorbed to sediments and thereafter not bioavailable.

Toxicity test and risk quotient results indicate the need for further risk characterization.

Fluridone

Fluridone (applied in pellet or liquid form) was not found to be definitively toxic or have Levels-of-Concern (LOC) exceedances for the three U.S. EPA species for water or sediment amphipod organisms. The peak concentration risk quotient for Stonewort did exceed an acute LOC. Fluridone was found to cause sublethal toxicity (decreased shoot and root length) to Typha. This indicated a potential for impacts on non-target plants.

Further risk characterization of fluridone impacts on non-target plants is warranted. There is also cause for concern over development of genetic resistance to fluridone which is emerging in plant populations in Florida.

Methoprene

Monitoring for methoprene is challenging because it is commonly applied to environments that do not lend themselves to traditional water and sediment sampling and testing methods (i.e. extremely shallow water and highly anoxic sediments). *In situ* and laboratory toxicity tests were completed, but the results were inconclusive. From the one site monitored for methoprene, water and porewater risk quotients indicated no need for further risk characterization. Methoprene was persistent in marsh sediments, up to the ppm level, for several weeks. Little methoprene sediment toxicity data could be located.

Future work is warranted to further characterize the risk of methoprene in sediments. Additional studies may also be warranted due to the common simultaneous application of methoprene and *Bacillus Thuringiensis israelensis* (BTi).

Triclopyr

Triclopyr was monitored at one location. Triclopyr peak concentration risk quotients showed no Levels-of-Concern exceedances. Triclopyr is often applied with a surfactant which may have much higher toxicity than the active ingredient.

Limited further triclopyr risk characterization is warranted. Risk characterizations are warranted when a surfactant is used with triclopyr.

Nonionic surfactants

The most commonly used surfactants at APMP monitoring sites were Target Prospreader Activator and R-11. Both are nonylphenolethoxylate based surfactants. Peak concentration risk quotients indicate Levels-of-Concern exceedances monitored at one location for a wide range of animal species including Delta Smelt and Sacramento Splittail. Vitellogenin induction experiments in Rainbow trout indicated that these nonylphenol surfactants can be an endocrine disruptor at application rates. There are a wide range of surfactants available, each one having a different toxicological profile. Due to their classification as an adjuvant, very little data is required for registration. Risk characterizations are warranted on all surfactants.

MANAGEMENT AND ASSESSMENT QUESTIONS REVISITED

The Management and Assessment questions developed at the beginning of the project were referred to throughout the planning and implementation of the APMP. Below is the analysis of how well the APMP addressed each Management question.

1. *Which aquatic pesticides used in California have the highest “risk” of impacts to people and the environment?* The literature review and field monitoring activities answered this question.
2. *What are the concentrations of the target aquatic pesticides in the environment (water, sediment, and biota) adjacent to their application point?* The field monitoring activities have begun to answer this question for the aquatic pesticides of interest.

Aquatic Pesticide Monitoring Program
Final Report

3. *Are the measured concentrations above existing effects thresholds?* This question has been answered for the sites studied by comparison of collected field data with published effects thresholds.
4. *Which locations have the highest “risk” of beneficial use impairment?* This question was not specifically addressed as it was a sufficient challenge to find sites suitable for monitoring that met the other selection criteria. Bioassessment data indicated that all locations samples may be degraded.
5. *What is the degree of biological impacts to non-target biota from application and exposure to aquatic pesticides?* The bioassessment and special toxicity tests performed addressed this question.
6. *What Best Management Practices are currently being used to mitigate potential impacts from aquatic pesticide application?* Pesticide application BMPs were not evaluated as part of this project. Non-chemical pest control alternatives have been studied extensively.

REFERENCES

Barbour, M.T., J. Gerritsen, B.D. Snyder, and J.B. Stribling. 1999. Rapid Bioassessment Protocols for Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinvertebrates and Fish, Second Edition. EPA 841-B-99-002. U.S. Environmental Protection Agency; Office of Water; Washington, D.C.

Burkhart, C.A., and Stross, R.G. 1990. An Aquatic Bioassay of Herbicide Bleaching in the Charophyte Sporeling, *Nitella furcata*. *Journal of Aquatic Plant Management*, 28:50-51.

Canfield, T.J., Kemble, N.E., Brumbaugh, W.G., Dwyer, F.J., Ingersoll, C.G., and Fairchild, J.F. 1994 Use of Benthic Invertebrate Community Structure and Sediment Quality Triad to Evaluate Metal-Contaminated Sediment in the Upper Clark Fork River, Montana. *Environmental Toxicology and Chemistry*, 13, 1999-2012.

Chapman, P.M., Dexter, H.B., Anderson, H.B., and Power, E.A. 1991. Evaluation of Effects Associated with an Oil Platform Using Sediment Quality Criteria. *Environmental Toxicology and Chemistry*, 10, 407-424.

Kreis, R.G., Jr. 1988. Integrated Study of Exposure and Biological Effects of In-place Pollutants in the Detroit River, Michigan: An Upper Great Lakes Connecting Channel. Final Report. U.S. Environmental Protection Agency, Duluth, MN

Suedel, B.C., Deaver, E., and Rodgers, J.H. Jr. 1996. Experimental Factors that may Affect Toxicity of Aqueous and Sediment-Bound Copper to Freshwater Organisms. *Archives of Environmental Contamination and Toxicology*, 30, 40-46.

U.S. Environmental Protection Agency. 2003. Biological Indicators of Watershed Health at: <http://www.epa.gov/bioindicators/html/indicator.html>

U.S. Environmental Protection Agency. 2003a. Toxicological Review of Acrolein. EPA/635/R-03/003. Washington DC.

U.S. Environmental Protection Agency. 1998. A Comparative Analysis of Ecological Risks from Pesticides, and Their Uses: Background, Methodology and Case Study. Office of Pesticide Programs, Washington DC.

U.S. Environmental Protection Agency. 1999. ECOFRAM Aquatic Report at: <http://www.epa.gov/oppefed1/ecorisk/aquareport.pdf>. Office of Pesticide Programs, Washington DC.

U.S. Environmental Protection Agency. 1982. Guidance for the Reregistration of Pesticide Products Containing Methoprene as the Active Ingredient. Office of Pesticide Programs, Washington, DC. pp.10-156

Aquatic Pesticide Monitoring Program
Final Report

Washington State Department of Ecology. 2001. Herbicide Risk Assessment for the Aquatic Plant Management Final Supplemental Environmental Impact Statement Appendix C Volume 3: 2,4-D. Publication Number 00-10-043

Yee, D., Siemering, G., Hayworth, J., and D. Oros. 2004. Aquatic Pesticide Monitoring Program Quality Assurance Program Plan. APMP Technical Report. SFEI Contribution #92. San Francisco Estuary Institute, Oakland, CA