Aquatic Pesticide Monitoring Program

Phase 2 (2003) Monitoring Project Report

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Phase 2 (2003) Monitoring Project Report
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EXECUTIVE SUMMARY

The Aquatic Pesticide Monitoring Program (APMP) began in January 2002 as the result of the 2001 U.S. Ninth Circuit Court of Appeals *Headwaters vs. Talent Irrigation District* and a related legal settlement between Waterkeepers of Northern California and the California State Water Resources Control Board (SWRCB). In the settlement, the SWRCB agreed to fund the San Francisco Estuary Institute (SFEI) to conduct two years of research and monitoring to: 1) provide the state with information to assist in development of the NPDES permits when the current emergency permit expires and, 2) explore non-chemical aquatic pest control alternatives. The contract between SFEI and the SWRCB specified the following studies:

- Fate and transport analysis of applied materials.
- Efforts to assess impacts to beneficial uses.
- Characterization of possible pesticide accumulation in sediments.
- Characterization of possible accumulation in organisms.
- Evaluate the cumulative impact of the pesticide use on non-target plants or animals.
- Conduct or monitor pilot projects for promising aquatic pesticide alternatives.

To accomplish the project goals, SFEI established a steering committee with representatives of all the stakeholders involved in aquatic pest control and several technical workgroups. The workgroups included: a chemical methods and toxicology workgroup, a modeling workgroup, a bioassessments workgroup and a non-chemical analysis workgroup. These workgroups consisted of scientists who have specific technical knowledge and SFEI staff. In addition, an independent peer review panel (Technical Review Group or TRG) of nationally recognized pesticide experts was established to provide outside review and feedback for the program.

The aquatic pesticide alternative project consisted of an extensive literature review, development of a cost effectiveness evaluation tool, and several pilot projects to

showcase new technologies or closely study older ones. The results of these efforts are documented in separate reports.

A tiered monitoring approach was implemented to help the program focus its resources appropriately. The three tiers were as follows:

Tier 1. Use the literature review to identify pesticide/environmental couplings where aquatic pesticide accumulation and potential effects are likely and unlikely.

Tier 2. Conduct sampling to confirm presence or absence of pesticides in the aquatic environment. Monitoring consisted of water, sediment, and tissue analysis for pesticide concentrations. Standard water and sediment toxicity tests were also conducted to assess aquatic biota impacts.

Tier 3. Utilize endocrine disruption assays, macroinvertebrate and plankton bioassessments, California listed species toxicity data endpoints, *in situ* toxicity tests, and sublethal toxicity effects to more fully characterize aquatic pesticide environmental impacts. Develop pesticide data sets for input into screening and assessment models to evaluate their efficacy in predicting pesticide behavior in the environment.

During the first year of the APMP, work focused on acrolein, fluridone, glyphosate and copper sulfate due to either their widespread use or high level of concern. During the second year of the APMP monitoring was conducted on pesticides of interest in the first year and applications of 2,4-D, diquat dibromide, triclopyr, chelated copper and methoprene. These nine pesticides were selected for monitoring based on input from the steering committee and the number of entities registered to use them. Some pesticides were not monitored due to extremely limited use or unavailability of analytical methods.

A literature review (Tier 1) was conducted for most pesticides in the first year (Phase 1) with additions and revisions continuing through the second year (Phase 2). Tier 2 monitoring was conducted at four sites in 2002 and then at 15 sites in 2003. All Tier 3 work was conducted in 2003. Sampling was conducted between March and October 2003, and was coordinated with individual organizations applying selected

pesticides in different settings These sites were selected in order to sample in a selection of water body types, pesticide user groups, and geographic distribution.

Water and sediment toxicity test and chemical characterization results were reviewed for trends in toxicity that may indicate impacts due to aquatic pesticide applications. Bioassessment results, endocrine disruption study results and the modeling efforts are documented in separate reports.

In order to provide a risk potential framework for the pesticide concentration results, risk quotients were calculated and compared to aquatic plant and animal Levels of Concern (LOCs) according to USEPA methods. 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.

Use of the limited data gathered during the two pesticide application seasons that the APMP has existed should be limited to screening purposes only to identify where further risk characterization or research may be needed. APMP is not yet of sufficient spatial or temporal extent to directly inform regulatory change. Due to the limited time and budget of the project, no definitive conclusions can be drawn from the data accumulated to date. APMP generated chemical characterization, toxicity, and bioassessment data. The chemical characterization and toxicity data can be used for screening purposes. In complex field situations, bioassessments require multiple years of data before even preliminary conclusions can be drawn from them.

The risk quotients and toxicity test results indicate that there are still considerable questions remaining before full risk characterizations of the aquatic pesticides of interest can be considered complete. Only the applications of glyphosate and triclopyr triethylamine salt alone appear to not warrant further risk characterization. All applications of pesticides with surfactants need further characterization.

For acrolein, it was not possible to accurately conduct standard toxicity testing on acrolein treated water. Phase 1 results showed that standard field sampling methods were insufficient. During Phase 2, an in-field derivitization process was developed that will

allow acrolein treated water samples to be collected, transported, and analyzed with reasonable accuracy. These methods will be further refined in Phase 3.

Further risk characterization will be continued into the third year of the APMP (Phase 3). Phase 3 work will focus on more in depth characterizations on a limited number of water bodies.

INTRODUCTION

Background

This is the Phase 2 (2003) project report of the Aquatic Pesticide Monitoring Program (APMP). This report covers the organization of APMP, reviews the efforts made in Phase 1 (2002), discusses in detail the Phase 2 (2003) monitoring efforts, and the work planned for Phase 3 (2004). A detailed discussion of only the Phase 2 (2003) results is made in this report. The results of Phase 1 (2002) monitoring are discussed thoroughly in the APMP Phase 1 (2002) Project Report available from SFEI. (Siemering, Hayworth *et al.* 2003)

The APMP began in January 2002 and is funded by the California State Water Resources Control Board (SWRCB). The APMP was begun because of a series of court decisions and legal settlement. 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 U.S. In order to keep the aquatic pesticide users legal under the recent court decision, the SWRCB issued an emergency permit in July 2002. However, the advocacy group Waterkeepers felt that this permit did not require adequate monitoring and challenged the permit in court. As a settlement with Waterkeepers, the SWRCB agreed to fund two years of research and monitoring to: 1) provide the state with enough information to develop an acceptable general NPDES permit when the current emergency permit expires and, 2) explore non-chemical aquatic pest control alternatives. The APMP is charged with developing, implementing, and managing a statewide aquatic pesticide monitoring program. The San Francisco Estuary Institute (SFEI), as the entity designated to implement the APMP, is administering the program under a contract with the SWRCB.

In late December 2003, SWRCB staff began the process of writing new NPDES permits to govern the discharge of aquatic pesticides. The results of the APMP

contributed to the development of these permits. The SWRCB has granted the APMP a contract extension to utilize funds not expended during the first two years of the project. Although the results of this third year of monitoring will not be available for the current round of permits, it will serve to inform the SWRCB when the next version of these aquatic pesticide NPDES permits are written.

Objectives

The purpose of the APMP is to provide information to the SWRCB and the Regional Water Quality Control Boards to assist in the development of NPDES permits to regulate discharges of aquatic pesticides to surface waters. The APMP management objectives include:

1. Conduct studies to evaluate the potential water quality impacts associated with the application of aquatic pesticides in representative water bodies throughout the State of California,
2. Evaluate the effectiveness and feasibility of nonchemical aquatic pest control alternatives.

The studies performed to evaluate potential pesticide impacts will hereafter be referred to in general as monitoring. 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 would be more precisely described as preliminary case study investigations performed with a wide variety of scientific tools to help inform the development of aquatic pesticide NPDES permits.

<u>Monitoring Programs</u>

To help guide the monitoring effort development, Management and Assessment questions were agreed to at the outset of the APMP. Management questions are the 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 are 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?*
    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?
6. *What Best Management Practices are currently being used to mitigate potential impacts from aquatic pesticide application?*
    a. Do pesticide label application instructions prevent impacts?
    b. Are there other BMPs that should be considered?

The Management and Assessment questions, generated through numerous discussions, were used to develop a plan of action for monitoring aquatic pesticide use. In addition to the Management and Assessment questions, the contract between the SWRCB and SFEI specifies the inclusion of the following studies:

- Fate and transport analysis of applied materials. Through literature review and field monitoring, this effort shall assess the fate and residence time of the pesticide in the environment and its movement through the ecosystem. This analysis shall evaluate and confirm through sampling the expected aerial extent and duration of the pesticide's presence, mass loading of the pesticide, and an evaluation of the pesticide's ability to persist or bio-accumulate. This analysis shall also apply to pesticide breakdown products.
- Efforts to assess 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.
- Characterization of accumulation in sediments where a pesticide may reasonably be suspected to be persistent in the environment. Sampling should include associated sediment quality parameters that may influence persistence or toxicity.
- Characterization of accumulation in organisms where a pesticide may reasonably be suspected to be persistent or bioaccumulative.

- Community monitoring survey. The goal of this study is to evaluate the cumulative impact of the pesticide use on non-target plants or animals. This study shall evaluate the impact of pesticide applications on organism diversity and ecosystem integrity relative to similar ecosystems where the applications do not occur.

Aquatic Pesticide Alternatives

In addition to the specific objectives outlined above to guide the APMP chemical monitoring portion, the contract between SFEI and the SWRCB also specified:

- Pilot projects for promising alternatives may be conducted and monitored to evaluate non-chemical pest control methods that may provide a practicable substitute for pesticide application.

The non-chemical aquatic pest control portion of the APMP worked to determine the feasibility non-chemical alternatives to chemical control in California waters. The focus was on rigorous, scientifically defensible assessments of projects in California waters already underway or pilot projects planned and executed by SFEI staff or subcontractors. These projects were conducted, where possible, in parallel to similar water bodies treated with chemical pesticides.

The usefulness of non-chemical approaches in various conditions was determined by quantitatively comparing their economic and environmental impacts. To determine economic feasibility, cost effectiveness analyses were conducted for chemical versus non-chemical alternatives for a select number of sites. Environmental factors for study were selected based on current knowledge gaps and regulatory concerns. Potential research areas included: a) effectiveness of nuisance vegetation removal, b) adverse effects on local animal communities, c) effects on water chemistry (e.g. dissolved oxygen, nutrients), and d) whether a particular method spreads invasive species. For each site and method, the factors to be compared depended on local information needs and the feasibility at that particular site.

The goals of the non-chemical alternatives project were to conduct an extensive review of nonchemical control methods, develop a cost effectiveness tool (in the form of

a report) that individuals needing to control aquatic pests can use to identify which non-chemical methods might be most appropriate for their particular situation, and conduct a number of demonstration projects to obtain cost and scientific data on the treatment of California water bodies. The results from this part of the APMP will be presented in the Greenfield *et al.* 2003, SFEI *et al.* 2003, and Mann and Wittman 2003.

Organization

An organizational flow chart is shown in **Figure 1**. The APMP is composed of a Steering Committee, Technical Review Group, contract analytical labs, and several focused workgroups that addressed questions relating to chemistry, toxicity, modeling, bioassessments and the use of non-chemical alternatives. The goals and responsibilities of the various committees and workgroups are described in detail below.

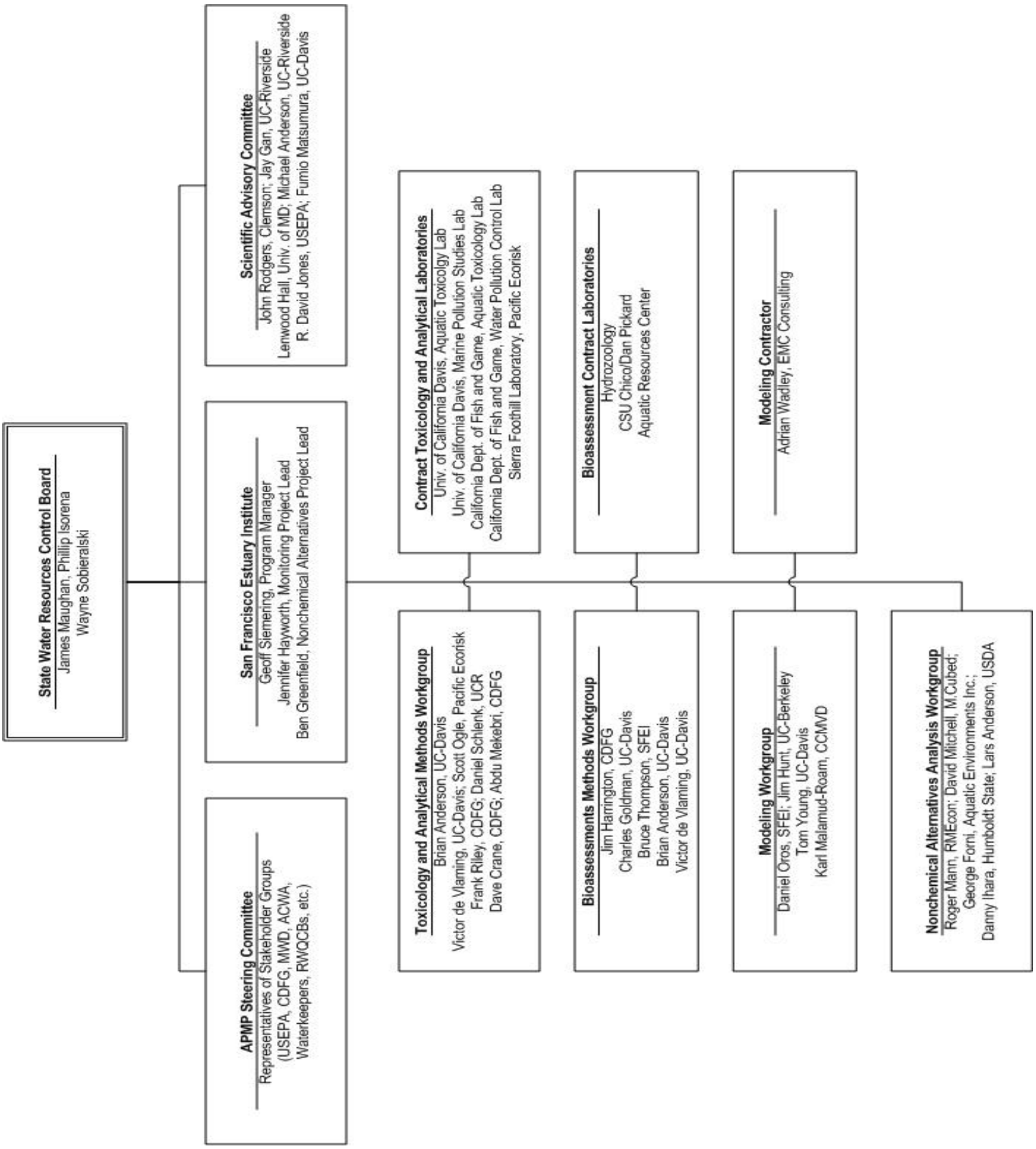


Figure 1. APMP Organizational Structure

Steering Committee

The Steering Committee is charged with overseeing and directing all components of the APMP. The committee is composed of individuals from Federal and State agencies, stakeholder groups, and public interests groups. During Phase 1 (2002) the Steering Committee meetings focused on creating an organizational structure for the APMP and guiding the development of the monitoring plans and non-chemical alternatives project. Subsequent Steering Committee meetings have focused on discussing and resolving programmatic development issues. The steering committee met monthly through June 2002 and quarterly thereafter. Steering committee members and alternates are listed in **Table 1**.

Table 1. Steering Committee Member List

First Name	Affiliation	First Name	Affiliation
Emily Alejandrino	RWQCB V	Vicki Kramer	CA Dept of Health Svs
Lars Anderson	US Dept. of Agriculture	Karl Malamud-Roam	Contra Costa Mosquito Vector Control District
Jim Atherstone	South San Joaquin Irrigation District	Tom Mauer	US Fish & Wildlife Service
Larry Bezark	Dept. of Food and Agriculture	Jim Maughan	SWRCB DWQ
David Bolland	Association of CA Water Agencies	Don McPeck	Orange County Public Facilities Dept
Geoff Brosseau	BASMAA	Markus Meier	EMC Environmental Consulting Svs.
Kathy Brunetti	California Dept. of Pesticide Regulation	Mike Messina	Solano Irrigation
Marcia Carlock	Dept. of Boating and Waterways	Elizabeth Miller-Jennings	SWRCB
Sejal Choksi	SF Baykeeper	Mark Novak.	Vector-Borne Disease Section (VBDS),
Susan Damron	Los Angeles Dept of Water & Power	Ross O'Connell	CA Dept of Food and Agriculture
Debra Denton	USEPA Region 9	Julie Owen	Dept. of Boating and Waterways
Joe Dillon	NMFS	Pankaj Parekh	Los Angeles Dept of Water & Power
Brian Finlayson	CA Department of Fish & Game	Mark Quisenberry	Sutter County Agriculture
Kathleen Goforth	US EPA, Region 9 (WTR5)	Rudy Schnagl	RWQCB V
Kean Goh	California Dept. of Pesticide Regulation	Wayne Sobieralski	SWRCB/DWQ
Larry Grabow	Marin Municipal Water District	John Stroh	San Joaquin County MVCD
Jasper Hempel	CA Water Quality Coalition	Bill Taylor	Metropolitan Water District of S. Calif.
John Hewitt	California Farm Bureau Federation	Bruce Thompson	San Francisco Estuary Institute
Phil Isorena	SWRCB	Marcia Torobin	MWASC
Bill Jennings	Delta Keeper	Craig Wilson	SWRCB (SWAMP)
Dennis Kelly	Syngenta	Darla Wise	Ventura County Water Protection District

Technical Review Group

The Technical Review Group (TRG) is composed of five scientists who are recognized as experts on pesticides and their effects. The responsibility of the TRG is to provide independent peer review for APMP workplans and findings. The TRG will meet four times: to review the Phase 1 (2002) draft monitoring plans, to review the results and interpretations of the Phase 1 (2002) monitoring effort and plans for the Phase 2 (2003) monitoring effort, to review the results and interpretations of the Phase 2 (2003)

monitoring effort and plans for the Phase 3 (2004) monitoring effort, and once to review the final APMP monitoring results. The TRG members are consulted periodically as technical questions arise and receive written updates quarterly. TRG members are listed in **Table 2**.

Table 2. Technical Review Group Members

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

Chemical Characterization and Toxicology Workgroup

The Chemistry and Toxicology Workgroups formed in Phase 1 (2002) were merged into a single workgroup to be able to more effectively plan monitoring work and analyze the resulting data. The members of this workgroup are listed in **Table 3**. The Phase 1 (2002) work plans for the Chemistry Workgroup and Toxicology Workgroups are also summarized.

Table 3. Chemical Characterization and Toxicology Workgroup Members

Name	Affiliation
Dave Crane, Ph.D.	CA Department of Fish and Game Fish and Wildlife Water Pollution Control Laboratory
Abdu Mekebri, Ph.D.	CA Department of Fish and Game Fish and Wildlife Water Pollution Control Laboratory
Brian Anderson	Marine Pollution Studies Laboratory Dept. of Environmental Toxicology University of California, Davis
Scott Ogle, Ph.D.	Pacific EcoRisk Laboratories
Frank Riley	CA Dept. of Fish and Game Aquatic Toxicology Laboratory
Daniel Schlenk, Ph.D.	Dept of Environmental Sciences University of California-Riverside
Victor de Vlaming, Ph.D.	Aquatic Toxicology Laboratory University of California, Davis

This group was responsible for the following tasks:

Task 1: Refine sampling protocols based on results from Phase 1 (2002) results. Develop a sampling method for collection of acrolein containing samples.

Task 2: Develop and conduct special toxicity testing studies.

This included *Typha ssp.* seed germination studies, *Chironomus tentans* sediment toxicity tests, and in-situ *Hyallela azteca* toxicity testing. These tests were conducted in conjunction with specific sampling events.

Task 3: Interpretation of chemical analysis and toxicity testing analysis data.

The California Department of Fish and Game-Water Pollution Control Laboratory (CDFG–WPCL) continued to serve as the primary contract laboratory to conduct the chemical analysis of pesticides in APMP samples. Additional contract laboratories were used for water and sediment quality analyses. The CDFG-WPCL and other contract labs have submitted the analytical methods standard operating procedures (SOPs), laboratory quality assurance and quality control (QA/QC) protocols.

Chemistry Workgroup

In Phase 1 (2002) the Chemistry Workgroup was established to identify and, if necessary, develop the laboratory methodology necessary to implement the aquatic pesticide sampling and monitoring program. The workgroup performed the following specific tasks during the Phase 1 (2002) monitoring effort:

Task 1. Review existing analytical methods.

A scientific literature review was conducted by SFEI and this information was provided to the Chemistry Workgroup (Siemering, David *et al.* 2003). The literature review was used by the workgroup to identify analytical methods that are currently used by the scientific community to evaluate aquatic pesticides and their degradation byproducts in aquatic matrices (water, sediments, and tissues). The literature review included information on analytical and environmental sampling methods, degradation byproducts and mechanisms, pesticide mixtures and formulations, persistence, fate, transport pathways, partitioning behavior between aquatic matrices (water, sediments, and tissue), environmental occurrence, and toxicity.

Task 2. Develop and apply current-use analytical methods.

The current-use analytical methods that are applied to determine aquatic pesticide levels and their degradation byproducts in water, sediment and tissue samples were evaluated. It was determined that methods currently available for analysis of the aquatic pesticides were sufficiently sensitive to meet APMP goals. The methods that were used for analyzing the target pesticides are shown in **Table 4**. More specific information on analytical methods may be found in the APMP QA plan.

Table 4. Chemical Methods Used for Pesticide Analysis.

Pesticide	Registrant	Medium	Method of Analysis
Acrolein	Baker Petrolite, Houston, Texas	Water	DNPH derivitization with HPLC-DAD (EPA Method 8315A modified)
Copper (sulfate and chelated)	Multiple registrants	Water	Atomic Absorption, furnace technique.
		Sediment	Atomic Absorption, flame and furnace techniques.
		Tissue	Atomic Absorption, flame and furnace techniques.
Fluridone	SePRO Corporation, Carmel, Indiana	Water	HPLC-DAD-Fluorescence or ELISA
		Sediment	Pressurized fluid extraction (PFE) with gel permeation chromatography cleanup followed by either HPLC-DAD-Fluorescence or HPLC-MS.
		Tissue	Pressurized fluid extraction (PFE) with gel permeation chromatography cleanup followed by either HPLC-DAD-Fluorescence or HPLC-MS.
Glyphosate	Monsanto (Aquamaster), St. Louis Missouri and Dow Agrochemicals (Rodeo), Indianapolis, Indiana	Water	EPA Method 547 Direct injection HPLC-Fluorescence with post column derivitization.
Diquat Dibromide	Syngenta, Basel Switzerland	Water	C8 extraction, ion-pair HPLC separation with diode array (DAD) / fluorescence detection
		Sediment & Tissue	Acid digestion, C8 extraction, ion-pair HPLC separation with diode array / fluorescence detection
Endothal	Elf Atofina Chemicals, Philadelphia, Pennsylvania	Water	Ion Exchange Extraction, Acidic Methanol Methylation and GC/Mass Spectrometry Certified EPA method 548.1.
Methoprene	Zoecon Corporation, Dallas, Texas	Water	EPA Method 3510C then LC/MSD: API-ES (negative)
		Sediment	ASE 200 Accelerated Solvent Extractor, then LC/MSD: Atmospheric Pressure Ionization-Electro Spray (positive mode)
2,4-D	Multiple Registrants	Water	Liquid-Solid Extraction and GC with Electron Capture Detector
		Sediment & Tissue	HPLC
Triclopyr	SePRO Corporation, Carmel, Indiana	Water	EPA 3535 then LC/MSD: API-ES (negative)
		Sediment	ASE 200 Accelerated Solvent Extractor, then LC/MSD: Atmospheric Pressure Ionization-Electro Spray (positive mode)
Nonionic Surfactant (nonylphenol ethoxylate-based)	Multiple registrants	Water	EPA 3535 then LC/MSD: API-ES (negative)
		Sediment	ASE 200 Accelerated Solvent Extractor, then LC/MSD: Atmospheric Pressure Ionization-Electro Spray (positive mode)

Task 3. Develop field sampling and handling procedures.

Field sampling, sample storage, and sample handling protocols were developed by the workgroup to ensure sample integrity.

Toxicity Workgroup

The Toxicity Workgroup was established to identify existing and, where necessary, develop new laboratory and field procedures appropriate for assessing toxicity of aquatic pesticides. Identification and development of methods for assessing toxicity of pesticides during Phase 1 proceeded as a multi-phase process that included the following tasks:

Task 1. Review of pesticide toxicity.

A scientific literature review was conducted by SFEI and this information was provided to the workgroup (Siemering, David *et al.* 2003). The literature review was used by the Toxicity Workgroup to identify analytical and toxicity testing methods that are currently used by the scientific community to evaluate aquatic pesticides and their degradation byproducts in aquatic matrices (water, sediment, and tissue). The literature review included information on analytical and environmental sampling methods, degradation products and mechanisms, pesticide mixtures and formulations, persistence, fate, transport pathways, partitioning behavior between aquatic matrices (water, sediment, and tissue), environmental occurrence, and toxicity. For the purpose of toxicity assessments, the literature review emphasized toxicity of pesticides to both standardized (U.S. EPA) test species and toxicity to appropriate resident or related species or genera.

Task 2. Identify and develop existing toxicity test procedures.

Existing methods used for the determination of aquatic pesticide toxicity were identified as part of the SFEI literature review and these were evaluated for their applicability for pesticide monitoring. Part of the evaluation process involved reviewing existing literature data to determine necessary analytical method minimum detection levels and identify where LC_{50} and threshold effect concentration data gaps existed. In addition to mortality, toxicity testing

emphasized sublethal endpoints where possible, and also incorporated biomarker endpoints where appropriate. When necessary, existing Toxicity Identification Evaluation procedures appropriate for determining causes of toxicity due to pesticides were also evaluated.

The workgroup recommended to APMP that water toxicity testing be conducted using standard U.S. EPA three species tests (water flea *Ceriodaphnia dubia*, fathead minnow *Pimephales promelas*, and green algae *Selenastrum capricornutum*) as well as larval Rainbow trout *Oncorhynchus mykiss*. It was also recommended that sediment toxicity testing use the amphipod species *Hyallela azteca*.

Task 3. Development of field sampling and handling procedures.

In cooperation with the Chemistry Workgroup, field sampling, sample storage and handling protocols were developed in order to insure the integrity of the collected field samples (water and sediments) for toxicity testing.

Bioassessment Workgroup

The Bioassessment Workgroup was established during Phase 2 (2003) to evaluate bioassessment data generated during the field season to develop sampling and sample analysis protocols for benthic, epiphytic, and phytoplankton bioassessment and to evaluate the data generated. Input from individual members was solicited through the 2003 field season and the entire workgroup convened in the fall of 2003 to evaluate the data generated. **Table 5** lists the members of the bioassessment workgroup.

Table 5. Bioassessment Workgroup Members

Name	Affiliation
Brian Anderson	Marine Pollution Studies Laboratory University of California, Davis
Bruce Thompson, Ph.D.	San Francisco Estuary Institute
Jim Harrington, Ph.D.	CA Department of Fish and Game Fish and Wildlife Water Pollution Control Laboratory
Charles Goldman, Ph.D.	Dept. of Environmental Science and Policy University of California-Davis
Victor de Vlaming, Ph.D.	Aquatic Toxicology Laboratory University of California, Davis

Modeling Workgroup

The Modeling Workgroup was established at the end of Phase 1 (2002) to evaluate and demonstrate the use of screening and assessment exposure models in the APMP to assist in determining the fate, transport, persistence, and exposure concentrations of pesticides in surface waters. The modeling component of the APMP is a special project funded to evaluate the efficacy of utilizing fate and transport models in the development of future discharger monitoring plans.

Several surface water screening and assessment models have been developed by the U.S. EPA and are currently available to the public (e.g., EXAMS, PRZM-EXAMS). The workgroup provided recommendations on which surface water screening and assessment model was to be used. The modeling information contributed to the understanding of aquatic pesticide fate, transport, persistence, and exposure concentrations of pesticides in surface waters. Once pesticide data (water concentrations and distributions) was collected, they were used to calibrate models for future use in designing discharger monitoring plans. **Table 6** lists the members of the modeling workgroup.

Table 6. Modeling Workgroup Members

Name	Affiliation
James Hunt, Ph.D.	Department of Civil and Environmental Engineering University of California, Berkeley
Karl Malamud-Roam, Ph.D.	Central Contra County Mosquito and Vector Control
Daniel Oros, Ph.D.	San Francisco Estuary Institute
Adrian Wadley	Eberhardt Meier Cassel Environmental Consulting Services
Tom Young, Ph.D.	Department of Civil and Environmental Engineering University of California, Davis

The Modeling Workgroup performed the following tasks in 2003:

Task 1. Review of models.

A literature review was conducted by Adrian Wadley and Daniel Oros and the information submitted to the workgroup. This information, included in the final technical report, was used to identify screening and assessment models that are currently used by the scientific community to evaluate aquatic pesticides and their degradation products in aquatic matrices (water, sediment, and tissue).

Task 2. Evaluate and recommend appropriate assessment models.

Screening and assessment models identified from the literature review were evaluated. The models that met the needs of the monitoring program were incorporated into the monitoring effort where it was feasible.

Task 3. Conduct pilot modeling studies.

The EXAMS II model was identified and pilot modeling studies conducted. Phase 2 (2003) data were used to calibrate and validate the model. Results of the pilot modeling were used for making recommendations to the APMP.

Task 4. Information dissemination.

A technical report was produced and submitted to the APMP (Wadley *et al.* 2003).

Pesticide Alternatives Workgroup

The Nonchemical Alternatives Workgroup is being developed to identify and confirm the viability of nonchemical pest control alternatives that are currently available for use in California and to evaluate the effectiveness and feasibility of nonchemical alternatives. Work on nonchemical pest control alternatives began in late 2002. This workgroup will accomplish it mission through administration of the following tasks during the Phase 2 monitoring effort. **Table 7** lists the members of the NCA Workgroup workgroup.

Table 7. Nonchemical Alternatives Workgroup Members

Name	Affiliation
Roger Mann, Ph.D.	Rmecon
David Mitchell	M. Cubed
George Forni	Aquatic Environments Incorporated
Danny Ihara, Ph.D.	Humboldt State University Center for Environmental Economic Development
Lars Anderson, Ph.D.	USDA-ARS Aquatic Weed Research Laboratory
Ben Greenfield	San Francisco Estuary Institute

Task 1. Conduct a literature review of nonchemical pest control alternatives and survey of nonchemical alternatives methods practitioners and researchers.

A literature review of nonchemical alternatives currently in commercial use and ones under development was used to identify which have a high potential for success in controlling aquatic pests in California where chemical pesticides are currently being used. Contacts were made with companies, agencies, and organizations involved in nonchemical aquatic pest control. In addition, efforts were made to contact experts outside of California to determine what methods are being used elsewhere in the U.S. that might not appear in the literature. The review also included a survey of permit and regulatory requirements for each nonchemical pest control scenario. This review (Greenfield *et al.* 2003) is available from SFEI.

Task 2. Participate in the design and execution of demonstration projects.

Demonstration projects were designed to test the effectiveness of several selected pesticide alternatives. These projects were conducted under real environmental conditions and in parallel to similar water bodies treated with chemical pesticides. Projects conducted were identified through a Request for Proposals. Projects were carried out entirely by subcontractors, as contractor and SFEI collaborations, and by SFEI in their entirety.

Task 3. Cost effectiveness analysis.

Cost effectiveness analyses were conducted on pesticide alternatives used in APMP demonstration projects or being conducted by other entities to compare to control using chemical methods. An integral part of such costs/benefit analyses

will include a comparison between the nonchemical control methods and chemical control methods. This work was carried out by workgroup members and by a research group from the University of California Santa Barbara's Bren School of Environmental Management.

Task 4. Information dissemination.

Reports detailing the results of demonstration projects (SFEI *et al.* 2004) and cost/benefit analyses (Mann and Wittman 2004) were provided to the SWRCB.

MONITORING PROGRAM

The sampling sites that were 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).

A tiered approach was developed to help focus the implementation of the aquatic pesticide monitoring effort. Three tiers were identified and are defined below. Tiers 1 and 2 were conducted during Phase 1 (2002) and Phase 2 (2003), while Tier 3 will be conducted during Phase 2 (2003) and Phase 3 (2004).

Tier 1. Use the literature review to identify pesticide/environmental couplings where aquatic pesticide accumulation is likely and unlikely.

Tier 2. Conduct a sampling program to confirm presence or absence of pesticides in the aquatic environment. Monitoring will consist of water, sediment, and tissue analysis for pesticide concentrations. Standard water and sediment toxicity tests will also be conducted to investigate the potential for aquatic biota impacts.

Tier 3. Utilize special studies, bioassessments, California listed species, and/or sublethal effects to more fully characterize aquatic pesticide environmental impacts where accumulation or effects are found or the literature indicates they may occur. These techniques would also be used to bridge data gaps in the existing science of the target aquatic 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. Information on these aquatic pesticides was collected through a detailed literature review conducted by SFEI, from the Department of Pesticide Regulation Pesticide Use Report database, and from the professional opinions of a subset of steering committee members. The target aquatic herbicides and their rankings were determined during 2002 and are shown in Table 8 of the Phase 1 (2002) Report (Siemering, Hayworth *et al.* 2003). Mosquito vector control compounds were not included in this initial ranking. The vector control compounds of interest were methoprene, malathion, and *Bacillus Thuringiensis israelensis* (Bti).

The regulatory areas that were considered for sampling included irrigation supply systems, drinking water reservoirs, exotic weed control (canals and coastal), mosquito abatement, flood control, drainage, and storm water, and recreational impoundments (golf courses and parks). A tiered approach was also developed with regard to water body types where sampling was practical. Increasingly complex water bodies were studied as the sampling methods were developed to adequately accommodate the specific system characteristics. This tiered approach is shown in **Table 8.**

In 2002, a database of aquatic pesticides NPDES permit holder was created. From this database, individual permit holders were identified whose water bodies 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 participating 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 visits and evaluations by APMP staff. While the greatest

number of sites possible were sampled, the number is still small in comparison to the total number of sites receiving aquatic pesticide applications within California.

Table 8. Water System Tiered Approach

Locales in order of increasing sampling difficulty
1. Irrigation District canals
2. Storm water canals or small streams
3. Small lakes or reservoirs
4. Delta
5. SF Bay or coastal estuaries

Phase 1(2002)

The APMP set several goals for the Phase 1 (2002) monitoring effort: 1) begin to gather data on aquatic pesticides that will help guide the SWRCB during the development of a general discharge permit for aquatic pesticide users, 2) perform chemical analysis and toxicity testing for a limited number of pesticides, 3) identify where gaps in scientific knowledge exist concerning the behavior of target pesticides in the environment, 4) close these gaps when possible, and 5) identify goals for the Phase 2 (2003) monitoring effort.

It was decided that APMP's Phase 1 initial monitoring efforts would be more efficiently achieved by closely coordinating with current aquatic pesticide users during their pesticide application cycle. By closely tying the monitoring efforts 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 is felt to be an appropriate approach.

Three of the final four pesticides monitored for during Phase 1 (acrolein, copper sulfate, and fluridone) were selected following the recommendations from the TRG. Glyphosate was added for monitoring in Phase 1 due to its' application in conjunction with a non-ionic surfactant, as well as an easily identified sampling location in Southern California. A total of six different water bodies were sampled in 2002.

Phase 2 (2003)

The APMP goals for the Phase 2 (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 number of study sites for priority pesticides, 4) implement bioassessment studies at all locations, 5) implement special sampling and

toxicity testing studies to identify where gaps in scientific knowledge exist concerning the behavior of target pesticides in the environment, 5) identify goals for the Phase 3 (2004) monitoring effort, 6) assemble and interpret data on aquatic pesticides behavior to assist the SWRCB in developing the NPDES permits for aquatic pesticide users.

Phase 2 monitoring continued the 'worst-case' sampling regime utilized in Phase 1. All pesticides of interest were monitored using this sampling regime. In addition to the chemical characterization and toxicity testing performed in Phase 1, the 'worst-case' regime was augmented with macroinvertebrate and phytoplankton bioassessment studies. These bioassessment studies allowed for a more comprehensive investigation of in-depth look into potential environmental impacts (chronic and acute) of aquatic pesticide applications.

Phase 2 (2003) studies also included the development of an in-field acrolein derivitization method, a pesticide and surfactant endocrine disruption study, and implementation of special toxicity testing studies. These studies were planned based on the results of Phase 1 (2002) investigations.

SAMPLING PROGRAM

Introduction

Phase 1 sampling was conducted in 2002 as a preliminary study of pesticide fate at selected sites for high priority pesticides. Measurements included chemistry and toxicity testing of water and sediment samples. The detailed sampling program for Phase 1 is discussed thoroughly in the APMP Phase 1 Report (Siemering, Hayworth *et al.* 2003).

Phase 2 monitoring in 2003 incorporated a triad sampling approach as 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 (US 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 is directly comparable. This work plan summarizes the objectives, technical approach, sampling methods, and schedules of the Phase 2 sampling program.

Objectives

The specific objectives of the monitoring are as follows:

1. Evaluate the acute lethal effects of pesticides on aquatic organisms through toxicity testing.
2. Evaluate the sublethal effects of pesticides on aquatic organisms. This entailed assessment of potential biochemical and/or physiological effects by toxicity testing.
3. Evaluate the effects of pesticides on non-target aquatic biological communities.
4. Determine the effect of repeated pesticide exposure on benthic macroinvertebrates. Community structure elements to be assessed include taxonomic, functional, and tolerance composition, along with abundance and diversity measures.
5. 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 to be 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.
6. Determine the effect of pesticide exposure on phytoplankton communities. Community structure elements to be assessed include taxonomic composition, abundance, and diversity measures.
7. Conduct experiments and collect data for calibration and validation of the EXAMSII fate and assessment model.

SAMPLING APPROACH

Sampling Strategy

Phase 2 monitoring sampled target aquatic pesticides from a diverse range of water-body types located in various regions throughout California. 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 during Phase 2 (2003) include 2,4-D, copper sulfate, chelated copper, diquat dibromide, fluridone, glyphosate, methoprene, and triclopyr. Due to the extremely volatile nature of acrolein, as seen from Phase 1 results, sampling for acrolein focused on developing field sampling methods to account for this volatility. Endothal was initially identified as a pesticide of interest, however, due to its very limited use in California, no monitoring of its' application was conducted. Also, monitoring for malathion was planned, but no application was made during the field season.

The sampling activities were organized into four tasks.

Task 1. Conduct intensive sampling utilizing the triad approach of target aquatic pesticides at twelve to fifteen sites throughout the state.

Sampling was conducted in conjunction with aquatic pesticide application by registered applicators. Most pesticides were monitored only on a short-term basis for no more than two weeks after direct application. The extent and level of bioassessment sampling were conducted as time and budget allow. Copper sulfate, fluridone, and glyphosate, identified as high priority pesticides, were sampled over a longer time period (up to 3-4 months after application) at a minimum of three locations that had repeated, single pesticide applications during the 2003 pesticide application season.

Task 2. Conduct special studies where appropriate, and as time and budget allow.

These studies included non-ionic surfactant analysis using endocrine system disruption assays, toxicity identification evaluations (TIEs), laboratory plant bioassays, and *in-situ* toxicity testing.

Task 3. Data analysis and interpretation.

Task 4. Draft and final report writing.

Sampling Program Design

To meet the objectives and provide consistency with Phase 1 sampling, a temporally stratified study design was implemented to coincide with pesticide application events. 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. Samples were collected before pesticide application and at various post application increments (**Table 9**). We conducted quantitative sampling to enable spatial and temporal statistical comparisons. Sampling locations throughout the state are shown graphically in **Figure 2**. A graphic representation of sampling at a single site is shown in **Figure 3**.

Reference Locations

At each location where monitoring took place, a reference site was identified. The ideal reference site sought was an identical water body immediately adjacent to the treated water body that had never received applications. This ideal was able to be achieved for only one Marin Municipal Water District reservoir couplet.

Reference sites were selected that were as similar as possible to the treated sites as possible minus 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. Every attempt was made to select sites with minimal inputs in addition to the aquatic pesticide.

Table 9. 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]

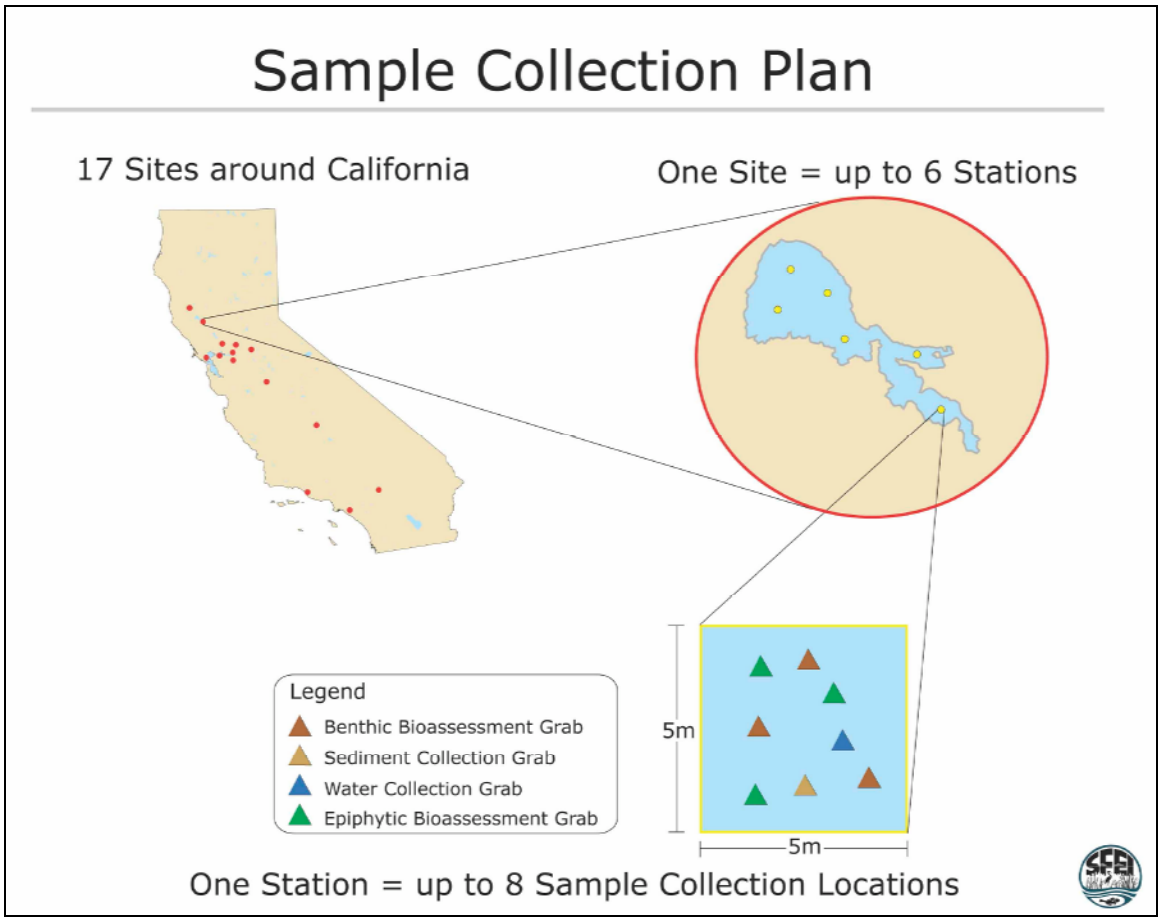
Order of Sample Collection
1. Physical Habitat Assessment
2. Water Quality Parameters
3. Macrophyte Survey
4. Sediment Parameters
5. Macroinvertebrate Assessments

Sampling Sites
Cooperating Permit Holder /Treated Sites /Control Site / Pesticide
Marin Municipal Water District / Bon Tempe and Nicasio Reservoirs / Lake Lagunitas / copper sulfate[3]
Cal. Dept. of Food and Agriculture / Costa Ponds / untreated pond / liquid fluridone[3]
U.S. FWS and Dept. of Boating and Waterways / Lower Stone Lake / Upper Stone Lake / glyphosate[3]
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 / granular fluridone
Contra Costa Mosquito Vector Control District / VCD pond / untreated area / methoprene
Merced Irrigation District / Atwater Canal / untreated canal section / glyphosate
Merced Irrigation District / LeGrande & Planada 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 / 7 Mile slough / untreated slough area / diquat dibromide

[1] Macrophytes and macroinvertebrates not collected at this time.
[2] For long-term sampling of copper sulfate, fluridone, and glyphosate only.
[3] Long-term study sites.

Figure 2. Phase 2 (2003) Sampling Locations.

Figure 3. Typical Sampling Plan for an Individual Site



Detailed Site Descriptions

Bon Tempe/ Lagunitas Reservoirs

Bon Tempe and Lagunitas reservoirs are located in the Mount Tam watershed near the town of Ross. In the Marin Water System, Bon Tempe is considered a medium size reservoir. Both reservoirs are filled during the wet season by runoff from a protected watershed and beyond air deposition. Lagunitas is located slightly higher in elevation and feeds into Bon Tempe. Bon Tempe reservoir (4000 acre feet) was constructed in 1949 and the Lagunitas reservoir (350 acre feet) was created in 1925.

Bon Tempe reservoir is treated with granular copper sulphate to control benthic algae. The copper sulphate is distributed via a boat-mounted hopper. Only select near shore areas where algae concentrations are known to be highest are treated. Treatment

occurs 1-3 times a season. Lagunitas has not been treated for at least 30 years although may have been treated early in its history.

Nicasio Reservoir

Located in the West Marin Watershed near the town of Nicasio. Nicasio is the second largest reservoir in the Marin system and there is limited agricultural development within its watershed boundaries. It is 100 feet at its deepest point near the dam and water siphon. The reservoir averages 20 feet deep and contains 22,400 acre feet. It is treated with dissolved copper sulphate to control floating algae. Treatment is only made in the arm of the reservoir nearest the dam where wind patterns cause the highest algae concentration. Treatment occurs approximately every four weeks during the summer months.

Byrnes Canal

Byrnes canal, near Fairfield, is operated by the Solano Irrigation District. It is a primary feed canal from which water is draw into lateral canals and onto farm fields. There are spillways into natural drainage systems, but these are only used when there is too much flow in the canal for the amount being drawn by growers in the area. The canal bottom is partially concrete lined (near canal structures), but otherwise unlined. The source of this water is Lake Berryessa and it is transported to the Byrnes canal in open canals and underground culverts. The canal parallels a highly traveled road for several miles and there are housing developments across the road from the canal. The canal sides are usually either lined with concrete or rip-rap. The canal is treated with chelated copper for macrophyte control once a month during the irrigation season. The chelated copper is injected into the canal system as the canal emerges from a culvert and flows over a spillway. Complete mixing occurs within a few hundred feet downstream of the injection point.

Potter Valley ID canal

The Potter Valley Irrigation District maintains a two-forked primary canal fed from the East Fork of the Russian River. Water is drawn from this canal into lateral canals and then onto grower's fields. The canals are dirt lined and fairly shallow, at highest flow reaching < 3 feet per second. Potter Valley ID is located northwest of Clear

Lake and the surrounding area is primarily used for cattle grazing. The canal is treated with chelated copper twice during the summer to control macrophytes and filamentous algae.

Swanton's Marsh

Swanton's marsh is both a natural and reconstructed wetland area near the Tesoro oil refinery, Martinez, and in the area of the Benicia bridge. The actual marsh area was previously a marina that was allowed to return to its natural state over a period of several decades. The marsh is on state land that is open to the public, but access is via a road controlled by the Tesoro refinery. This marsh is bordered on the western edge by other marshes owned by Tesoro and on the eastern edge by marshes within the Concord Naval Weapons station. The marsh is fed from inland streams and is strongly tidally influenced. The water feeding the march flows through upland marshes that are also treated for mosquito control. Swanton's marsh is treated frequently throughout the summer months for mosquito control with methoprene and *Bacillus thuringiensis israelensis*. Application is made with sprayer mounted on an amphibious vehicle and with hand sprayers.

Sand Bay Isle

Sand Bay Isle Homeowners Association maintains two small ponds within their development. San Bay is located between Stockton and Brentwood near State Highway 4. The ponds average five feet deep and are each approximately 250 feet in diameter. The ponds are surrounded by condominiums and a small amount of lawn area with the shoreline covered with rip-rap. The ponds are fed by groundwater and have only one outlet. They are treated with diquat dibromide and copper sulphate to control sago pondweed. The diquat dibromide application occurs early in the season and the copper sulphate treatment in mid summer.

Costa Ponds

Costa Ponds are several small lakes (the largest is 5 acres) located near Porterville at the base of Sierra Nevada foothills. The lakes were constructed as a fishing resort and are surrounded by dry scrub and limited vegetation. The source of the water is the Tule River. No outboard motors are allowed in the ponds and there are no uncontrolled inputs. The ponds average nine feet in depth. The larger ponds are treated with fluridone one to

two times a season for macrophyte control. The smallest pond is not treated. Water flows through the ponds in series beginning with the smallest pond.

Big Bear Lake

Big Bear Lake is located in the San Bernardino Mountains and currently holds 35,000 acre feet of water. Originally constructed in 1881 to store water for irrigation of crops in Redlands, in 1977 the dam, lake bottom and surface water rights were acquired by the local landowners and the Big Bear Municipal Water District was formed. Since 1977 the water level in the lake has been managed to ensure recreational opportunities with any remaining irrigation needs met by Metropolitan Water District sources (which can include lake water). Big Bear Lake is fed by snowmelt and groundwater. The lake is used heavily for recreation purposes and is ringed with vacation homes and ski slopes. The lake surface sometimes freezes during the winter.

For the past two years granular fluridone has been used to treat the shallower parts of the lake to control milfoil. Mechanical harvesting was conducted for 15 years prior to the fluridone use. Fluridone treatments and milfoil harvesting occurs in the near-shore areas to a depth of approximately nine feet.

Doris Drain

Doris Drain is a flood control canal in Ventura. The canal is several miles long and terminates into a larger canal near the ocean. During the dry season, water flows in the canal come only from runoff from the surrounding fields. The drainage comes from tile drains installed in the surrounding fields, although during the rainy season direct runoff is likely. The sides of the canal are covered with a mixture of rip-rap, gravel, and concrete. The channel bottom is rock and sediment. The crops in this area are primarily strawberries and sod.

The canal is treated with glyphosate 2-3 times a season for weed control along the banks and channel bottom. Treatment is made with a truck mounted sprayer arm. One bank of the canal is left untreated to maintain animal habitat.

Bear Creek

Bear Creek is located between Jackson and Lodi in the low foothills. It is a natural creek surrounded by grazing lands. Flow in the creek is low in the area treated

due to the construction of several beaver dams. The creek bottom is primarily cobblestone with little sediment. The creek was treated with triclopyr this year to control macrophytes. This application was made by California Department of Food and Agriculture using a research permit for triclopyr.

Stone Lake National Wildlife Refuge

Stone Lake National Wildlife Refuge is located approximately 15 minutes south of Sacramento on I-5 just south of Elk Grove. The lake is fed by water from the Sacramento River. The water passes through the lakes and then is returned to the Sacramento River. There is a small dam that controls the lake level. The dam dampens the tidal flow in the lake. Additional input into northern Stone Lake comes from storm water drainages from nearby housing developments. Water is drawn from the lake from nearby growers for irrigation. The western lake edge is protected by levees, but direct runoff may occur from other fields.

The lake is treated with 2,4-D and glyphosate (both with surfactant added) to control primarily water hyacinth, but the lake is also infested with Eurasian milfoil. Treatment occurs frequently during the summer months. 2,4-D use is restricted until later in the summer. The sampling was conducted in solely in Southern Stone Lake.

7 Mile Slough

7 Mile slough is a Delta slough treated by DBW with diquat dibromide to control dense submerged mats of *Egeria densa* and parrot feather. The site is tidally influenced and receives inputs from agricultural drainage and heavy boat traffic discharges.

Atwater Canal

The Atwater Canal is part of the Merced Irrigation District system. The canal water is used for crop irrigation, but not all the water ends up on crop fields. The primary source of water is from the Atwater water treatment plant, but it does receive runoff during the rainy season. The canal averages 8-10 feet wide and 2-3 feet deep. The canal is treated with glyphosate once in the early fall to control plants along the canal banks and growing on the canal bottom. Glyphosate application is made with a sprayer mounted on a truck and hand spraying.

LeGrande & Planada Canal

The LeGrande & Planada Canal is part of the Merced Irrigation District system fed by Merced River water. The LeGrande & Planada canal receives water from Lake Yosemite which, in turn, is filled by the MID Main Canal. The Planada canal is a significant lateral canal off of the LeGrande Canal. This canal is approximately 20 feet wide and 10 feet deep at its' head and narrows as it flows downstream. Water from this canal is used for crop irrigation. The canal is treated with acrolein several times during the growing season for macrophyte control.

Sample Collection Methods

Protocols for chemistry and toxicity sampling and handling have been previously compiled in the Aquatic Pesticide Monitoring Program Quality Assurance Project Plan (QAPP) (Yee *et al.* 2004) and in the APMP Phase 1 (2002) Annual Report (Siemering, Hayworth *et al.* 2003). Modeling pilot studies utilized the protocols developed for chemical characterization and toxicity testing sampling.

Sampling for bioassessments was conducted according to aquatic system type (moving water versus still water) and target biological community. The California Department of Fish and Game has developed sampling protocols for both lentic and lotic systems (CDFG 1999 and 2002), and these were adapted and used. The bioassessment methods and results are detailed in Hayworth *et al.* 2004.

Special Studies

Special studies included analysis of potential surfactant endocrine system disruption, toxicity identification evaluations (TIEs) for individual pesticides where needed, laboratory plant bioassays, and *in-situ* toxicity testing. Most of the studies were conducted in the laboratory, with the exception of some in-situ testing and bioaccumulation tissue collection. Special studies were conducted as follows (**Table 10**):

Table 10. Special Studies

Study	**Target Pesticide**	**Test Species/ Method**	**Endpoint**
Plant Bioassay	Fluridone	*Typha spp.*	Early Seedling Growth
Endocrine Disruption Assays	diquat, glyphosate, triclopyr, 2,4-D, surfactants	Juvenile *O. mykiss*	Endocrine disruption
In-situ toxicity testing	Methoprene	*Hyallela azteca* (*in situ*), *Chironomus tetans* (in lab)	Morphological deformities, life-cycle disruptions, mortality
TIE	As needed	Determined at time of TIE	Varies
Model Pilot Evaluation Studies	Copper	Chemical characterization and dye study	

Plant Bioassays

Plant bioassays on fluridone treated sediment were conducted to determine potential acute and chronic toxicity effects on nontarget plants. A common emergent plant species (cattail, *Typha ssp.*) was used as the test organism using current experimental procedures provided by John Rodgers, Jr. (Clemson University).

In situ Toxicity Testing

In situ toxicity was monitored within a methoprene treatment area of the Contra Costa Municipal Vector Control District (CCMVCD). *In situ* toxicity tests were conducted with an amphipod, *Hyallela azteca*. Field exposures were either 96-h or 10-day toxicity tests. After 96 hours, one half of the test organisms were retrieved for analysis. The remaining 50% were retrieved after 10 days. Test organisms were also placed in a nearby untreated reference site. The methodology was based on USEPA standard *H. azteca* test methods and with modifications for field exposures described in Phillips et al. (2004)

Endocrine disruption assays

Pesticides in a tank mix with a surfactant were investigated with assay conducted to assess the potential for pesticide/surfactant-combinations to act as endocrine disrupting agents. Four APMP target pesticides commonly applied with surfactants: glyphosate, diquat dibromide, 2,4-D, and triclopyr. Two commercial surfactants (Target Prospreader

Activator and R-11) were tested because of their widespread use at APMP monitoring sites.

Toxicity Identification Evaluations (TIEs)

TIEs were planned on samples where toxicity was observed in water and sediment samples. TIEs were only performed where there was sufficient water or sediment available or when more sample could be obtained prior to additional contaminant inputs to a system. TIEs were only performed when there were sufficient scientific methods available. When TIEs were conducted, they were only performed to the point at which it could be determined if cause of toxicity was either the pesticide or nonionic surfactant. If it was determined that toxicity was not caused by the pesticide or surfactant, no further TIE work was done.

Model Validation Experiments

During the spring of 2003, the USEPA EXAMSII model was used to attempt to predict the behavior of chelated copper in an irrigation canal. The EXAMSII Model is suitable for use in aquatic systems with well-defined inputs and hydrodynamics. Detailed site information was collected to feed into the EXAMSII fate and assessment model, as reflected in the conventional parameters to be collected at every site (see Table 12). Field experiments using conservative tracer/dye were conducted at the Solano Irrigation District Burns canal. A conservative agent was added to the water column in concert with pesticide application in order to trace pesticide fate and transport in relation to the hydrodynamics of the system. The resulting data was then used to refine the model.

Data Management

All digital data and information generated from sampling are stored at SFEI and have been converted to standard APMP database format (QAP). The APMP database is in the SWAMP database format where formats exist for the types of data collected.

Data Interpretation

Water and sediment toxicity test and chemical characterization results were reviewed for trends in toxicity that may indicate impacts due to aquatic pesticide applications. In order to provide a risk potential framework for the pesticide

concentration results, risk quotients were calculated according to USEPA methods described below.

Fish and crayfish fluridone tissue concentrations results were compared to regulatory guidelines for human consumption. This data was generated in early 2003, but was unavailable for inclusion in the APMP Phase 1 report.

Risk Quotient Calculation

Risk quotients were calculated according the method promulgated by the USEPA (USEPA, 1998). These risk quotients are part of the first step of a four part risk characterization process outlined in the ECOFRAM draft Aquatic Report (USEPA, 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.

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: $RQ = {}^{Exposure}\!/\!_{Toxicity}$ (USEPA, 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 is meant to be protective, not predictive, and is 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 will not be undertaken in this report.

These RQs are then compared to a Level of Concern (LOC) determined by the USEPA Office of Pesticide Programs (OPP). The specific LOCs for aquatic animals and plants are shown in **Table 11**. LOCs are unit less values that allow for simple determination of possible exceedances of regulatory limits. An LOC exceedances is indicative only of the need for further investigation of an application scenario.

Table 11. 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 USEPA 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 will be used, as will values for any listed species present. Where there are multiple toxicity values for the same test species, the

lowest value will be selected. The toxicity measurements used are from peer-reviewed academic literature, FIFRA registration documents, or other government reports.

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

Results and Discussion

Bioassessment data is not discussed in this report and is available in a separate document (Hayworth *et al.* 2004).

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 nonylphenolethoxylate surfactant) to a main stem slough of South Stone Lake within the Stone Lake National Wildlife Refuge (SLNWR) on September 8, 2003. This 2,4-D is the formulation registered for aquatic use. Each of the different 2,4-D compounds have different toxicological properties and it is 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 by DBW staff using glyphosate. 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. Chemical characterization and toxicity samples for water and sediment, along with macroinvertebrate samples, were collected according to the sampling matrix in Appendix A.

Chemical characterization and toxicity results are shown in Appendix B. Chemistry results show 2,4-D present in most water and porewater samples prior to the pesticide application. Pre-application 2,4-D porewater concentrations were between 1.02-1.43 ppb and the water concentration was 0.14 ppb. Two and a half hours after

application, the 2,4-D concentrations in the water rose to 20-27.5 ppb. The calculated risk quotients for the maximum 2,4-D concentration detected in water did not exceed any LOCs (**Table 12**). However, the surfactant concentration was four times the acute endangered species LOC for Delta smelt (**Table 13**).

It is believed that the elevated pre-application chemistry concentrations indicate persistence from a prior or nearby application. The half-life of 2,4-D is approximately seven days in aquatic environments, and is affected by shifts in water quality conditions such as changes in sediment load, organic carbon and nutrient load (Siemering, David *et al.* 2003). As Stone Lake is influenced by heavy winds and muted tidal action, it is expected that daily shifts in sediment particulate distribution and drift within the lake and accounted for potentially patchy herbicide distribution and variance of 2,4-D persistence in our results.

Table 12. 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	*D. magna* LC50	0.0038	No
	100 mg/l	*P. promelas* LC50	0.000275	No
	128 mg/l	Delta smelt NOEC	0.000215	No

Table 13. 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	*C. dubia* LC50	0.004	No
	420 µg/l	*C. dubia* NOEC	0.05	No
	1100 µg/l	*P. promelas* LC50	0.02	No
	340 µg/l	*P. promelas* 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

Water toxicity to fathead minnow (*Pimephales promelas*) was observed pre-application and at 2.5 hrs post application. The UC-Davis Aquatic Toxicology Lab, which performed the tests, felt that this toxicity was likely due to a fish pathogen rather than the herbicide. The pathogen problem is what has been termed "Toxicity of

Unknown Cause" or TUC. It's a fairly wide-spread problem found not only in the Delta, but also out-of-state. It has typically been found in softer waters that have increased sediment or turbidity. It manifests on the 3rd or 4th day of static *P. promelas* tests as extremely varied mortality among the replicates and is not repeatable.

Sediment toxicity, in the form of growth impairment of *H. azteca*, was found in one pre-application sample 10-day test, although the 2,4-D concentration at this station was not elevated pre-application. The cause of this growth impairment is unclear. No sediment toxicity was observed in any samples collected two weeks after application.

Research has indicated that 2,4-D alone and in combination with a nonylphenol surfactant may cause endocrine disruption in juvenile *O. mykiss* at high label-approved application rates. Further work will be conducted in 2004 to further characterize the risk of this potential endocrine disruption.

Conclusion

Monitoring at Stone Lake NWR found no toxicity associated with the 2,4-D and nonylphenol surfactant applied. The risk quotients calculated from the peak 2,4-D water concentrations indicate no exceedances of LOCs, but the surfactant peak concentration did exceed the acute LOC for Delta smelt. 2,4-D's potential endocrine disrupting warrants further study (see endocrine disruption results section below). The R-11 surfactant may require further work based on its LOC exceedance for Delta smelt and for its' general endocrine disrupting properties.

Acrolein

Acrolein was monitored in the Livingston and Le Grande canal systems within the Merced Irrigation District in both Phase 1 and 2. Phase 1 results showed serious limitations in the field sampling methods normally used to collect water samples for pesticide analysis. Rapid degradation and volatilization make it necessary to stabilize acrolein-containing samples immediately after collection and prior to shipment to an analytical lab. Phase 2 efforts focused on the development of an *in situ* stabilization process that would allow for accurate collection and laboratory analysis of the highly volatile acrolein molecule as well as be simple enough for any competent field crew to

perform. The California Department Fish and Game Water Pollution Control Lab (CDFG-WPCL) developed such a method and APMP staff field tested its efficacy following an acrolein application in the MID Le Grande & Planada canal.

Goals for Acrolein Method Development and Validation

The stability of acrolein (2-propenal, CAS# 107-02-8) from sampling time to the time of extraction and analysis was explored to determine if a sampling method could be developed for acrolein in surface water. The methodology used for this study was a modified EPA Method 8315 where 2,4-dinitrophenylhydrazine (DNPH) is used to derivitize acrolein at the time of collection. The sample is then solvent extracted, evaporated and reconstituted for analysis by HPLC-MSD. The stability and analytical recovery of acrolein is dependant on several parameters. Acrolein is a volatile compound (molecular weight = 56) with a high potential for photolytic transformation (EPA 2003a). However, by derivitizing it at the sampling site, the compound is stabilized for a short period of time (approximately 24-48 hours) allowing the derivitized water sample to be transported to the laboratory for processing and analysis. During the study several questions arose and were also investigated. The following items were monitored and addressed in the research project:

1. Acrolein stability: Temperature, pH, sampling method, holding time.
2. DNPH stability and addition to acrolein: Shelf life of prepared DNPH solution, application time, volume and concentration required.
3. Acrolein metabolite: Formation of 3-HPA (3-hydroxypropanal, beta-hydropropionaldehyde, hydracrolein, reuterin).

Method Development Setup - Laboratory

Five gallon buckets containing ten liters of American River water were used. The temperature and pH of the water samples were monitored. Water with a pH of 6.4 at 22ºC (indoors) and 30ºC (outdoors) was used. Water sample aliquots were taken prior to the addition of acrolein and were used for blanks and laboratory control standards. Sub-samples were taken at time (t) equals 0 and 3 hours after addition of acrolein. Buckets were spiked with 0.5, 1.0 and 20 ppb acrolein levels. Two aliquots (500 mL each) were taken from each bucket at each time period (t=0 and t=3 hours) and one from each time

period was treated with 45 mL (1 g/L DNPH solution) and one was left untreated. All samples were refrigerated immediately. Samples were extracted at approximately 24, 72, 96 and 120 hours after collection.

The acrolein metabolite 3-HPA was made from a standard of 500 ppb acrolein in DI water. Initially, the acrolein standard was placed outside for three days and then brought inside the laboratory and stored at room temperature. Aliquots of the standard were periodically extracted and analyzed until the concentration of 3-HPA stabilized.

Method Validation Setup - Field

Field samples were obtained from the LeGrand & Planada Canal (Table 9) shortly after an acrolein application at the LeGrand Canal headgates. Samples were collected by submerging a wide mouth amber glass bottle until full, immediately decanting an amount equal to the amount of DNPH to be added, and then adding the DNPH. The bottle was then topped up with water collected in a second amber glass bottle to eliminate any headspace. In Phase 1, the samples were collected by pumping water into collection bottles. The Phase 1 method is the typical method for collecting water samples for pesticide concentration analysis, but lead to the loss of virtually all the acrolein in the samples.

The temperature and pH of the water samples were 19.7-22.7ºC with a pH range of 6.6-6.8. DNPH solution was prepared the afternoon of July 21, 2003 and given to field personnel with instructions. Field samples were taken the day following an application of acrolein. Multiple samples were collected at each site on July 23, 2003. Some samples were treated with DNPH immediately, while the others were delivered to the lab untreated. Control samples were taken at a different site in the irrigation system. All of the samples were kept cold and delivered to the laboratory the afternoon of the day they were collected. The samples were extracted immediately upon arrival at the laboratory.

Summary of Results

Preliminary laboratory results showed that water samples derivitized with DNPH immediately after sampling resulted in higher acrolein recoveries (or minimum loss of acrolein) compared to untreated samples. The results also showed that the DNPH treated samples need to be extracted as soon as possible after collection, not to exceed 48 hours

(see Table 14). Acrolein can be monitored and analyzed with a high degree of accuracy and precision using this method. Table 15 shows that the analysis of DNPH treated field samples confirmed this with a high degree of precision (0.3 - 0.9 % RSD) if the following conditions are met.

1. Acrolein stability: The range of temperature and pH of the water used for this study did not have a significant effect on the stability of acrolein. (T = 20-30ºC, pH = 6.4-7.0). The sampling method and holding time did have a significant effect on the stability of acrolein. Sampling with a wide mouth bottle reduced aeration of the compound. Large decreases in acrolein recovery (3-10 times) were demonstrated in untreated field water samples over a short period of time. Delaying the addition of DNPH to the water samples for as little as a few hours resulted in a large decrease in the recovery of acrolein. (See Table 14).

2. DNPH stability and addition to acrolein: DNPH solution must be prepared, kept cold and used within 24-48 hours. The solution must be added to the water at the time of sampling and the samples must be kept cold in order for acrolein to remain stable. After addition of DNPH, extraction must occur as soon as possible and should not exceed 48 hours. Once extracted, acrolein-DNPH is very stable. Addition of 45 mL (1 g/L DNPH) can derivitize one liter of water containing 1 mg/L concentrations of acrolein with 100 % efficiency (correlation factor = 0.9999%).

3. 3-HPA: One major metabolite of acrolein is 3-hydroxypropanal. This hydrolysis product is not available from any major U.S. supplier and must be made in the lab. 3-HPA formation begins quickly but takes a long time to obtain a high purity.

Table 14. Acrolein Water Concentrations with and without DNPH

Sample ID	Sample #	Acrolein (ppb)	3-HPA (ppb)
Pre-application Site			
Pre-01-01 no DNPH	1	ND	ND
Pre-01-01 w/DNPH	1	ND	ND
Pre-01-02 w/DNPH	2	0.023	ND
Site 1			
01-01 no DNPH	1	<RL	14.3
01-01-01 w/DNPH	1	0.046	47.3
01-01-02 w/DNPH	2	0.048	49.0
01-01-03 w/DNPH	3	0.042	41.2
Site 2			
01-02 no DNPH	1	<RL	41.7
01-02-01 w/DNPH	1	0.075	410
01-02-02 w/DNPH	2	0.090	430
01-02-03 w/DNPH	3	0.074	400

Table 15. Statistical Results for Acrolein Water Concentrations with and without DNPH

Pre-application Site	Sample #	Acrolein (ppb)	Average	RPE (%)	%	SD	± 3SD	LCL	UCL
Pre-01-01 w/DNPH	1	ND							
Pre-01-02 w/DNPH	2	0.023							
Site 1									
01-01-01 w/DNPH	1	0.046	0.045	1.5	99			0.036	0.054
01-01-02 w/DNPH	2	0.048	0.045	5.9	106	0.003	0.009	0.036	0.054
01-01-03 w/DNPH	3	0.042	0.045	7.4	93			0.036	0.054
Site 2									
01-02-01 w/DNPH	1	0.075	0.080	5.9	94			0.053	0.107
01-02-02 w/DNPH	2	0.090	0.080	13	113	0.009	0.027	0.053	0.107
01-02-03 w/DNPH	3	0.074	0.080	7.1	93			0.053	0.107

Analytical Set-up:

Acrolein and 3-HPA are analyzed by LC/MSD with the conditions shown in **Tables 16** and **17**.

Table 16. Acrolein Detection Chromatographic Conditions

Chromatographic Conditions	
Instrument:	Agilent LC/MSD 1100 Series
Column:	Agilent Zorbax C-18 column, 15cm x 4.6mm i.d. x 5µm
Mobile phase:	A: Water (1% methanol),
	B: Acetonitrile
Gradient:	Start with 10% B, hold for 0 min
	At 30 min 80% B, hold for 0 min
	At 32 min 10% B, hold for 0 min
Flow rate:	1.0 mL/min
Post time:	5 min
Column temp:	38ºC
Injection vol:	20 µL
Diode-array detector:	Signal: 360, 16; 254, 16nm
	Reference: 500, 20 nm

Table 17. Acrolein Detection MS Conditions

MS Conditions:	
Source:	APCI
Ionization mode:	Negative
Vcap:	1500 V
Corona current:	10 µA
Nebulizer:	50 psig
Drying gas flow:	5/min
Drying gas temp:	340ºC
Vaporizer temp:	485ºC
Selective Ion Monitoring (SIM)	
SIM 1:	m/z = 235 (acrolein)
SIM 2:	m/z = 237 (acetone)
SIM 3:	m/z = 253 (3-HPA)
Scan:	60-300
Threshold:	150 counts
Gain:	2
Step size:	0.1 amu
Peak width:	0.1 min
Time filter:	On
Fragmentor:	50 V

Quantification:

A standard curve is made from acrolein that has been freshly derivitized. The reporting limit is 0.020 ppb. Since the acrolein metabolite 3-HPA is not commercially available, 3-HPA concentrations were estimated by using a degraded acrolein standard

where the loss of acrolein is used as the concentration of the 3-HPA peak. Samples were analyzed in SIM mode and verified by extracted ion analysis.

Future Goals for Acrolein Method Validation

The future acrolein method validation goals will be continued after input from the TRG.

1. Adding small amounts of solvent (hexane or 70:30 hexane: dichloromethane) directly to derivitized field samples at the site should dramatically decrease the loss of acrolein and stabilize it for a longer period of time before analysis.
2. This method of determining the presence and concentration of acrolein in surface water appears to be very reliable. Recoveries of laboratory control standards and matrix spikes range from 80-85%. However, more samples need to be analyzed to validate the method statistically. While, laboratory samples are satisfactory to use, samples in buckets are static. Therefore, field samples are preferred to more accurately reflect real flow-through environmental conditions.
3. The purification of 3-HPA from acrolein is a continuing effort. Extractions need to be done periodically until the amount of decreased acrolein and increased 3-HPA is stable. In the meantime, we will continue to search for a supplier for this compound.

Conclusion

APMP work with acrolein this year focused on development of a field sampling method that would allow for accurate determination of concentrations in the environment. Toxicity testing is not possible with acrolein due to its rapid breakdown and volatilization. Since the LOEC/NOEC values for acrolein are in the sub parts per billion range, where acrolein is detected above those values it may be considered toxic and the most appropriate monitoring at this time would be chemical characterization only.

The current USEPA method has an adequate detection limit, however commonly used field sampling techniques are insufficient and will lead to erroneous analytical results. The in-field derivitization method developed by the APMP can be easily transferred to commercial labs and private consulting firms. QA round-robin exercises

would be needed to ensure accuracy with the new field sampling technique. Further work in 2004 will focus on improving the in-field derivitization beyond that achieved in 2003.

One additional consideration with acrolein is the fact that there is very limited data on acrolein's primary breakdown product, 3-hydroxypropanal. APMP plans on conducting more work on this compound in 2004.

Copper Sulfate

Copper sulfate was monitored during Phase 1 and 2 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 not sampled during Phase 2 and Lake Lagunitas was used as the sole reference site. 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 had copper treatment within the last 30 or more years. The sample matrix is shown in Appendix A, and the chemical and toxicological results are in Appendix C. Chemistry and toxicity results for Phase 2 were assessed using the same methodology as employed in Phase 1.

Bon Tempe reservoir was treated on June 27, 2003. Copper concentrations in sediment porewater ranged from 0.0016-2.37 mg/L (dissolved copper) and 338-1880 mg/L (dry weight) in the sediment. These values are consistent with those found during Phase 1 sampling. Of note, is that some pre-application concentrations are as high as the post-application values. This was expected as copper is sequestered in sediment and there is little sediment transport within the reservoir. Station B02 had the highest

sediment copper concentration. According to MMWD staff, this area of the lake is particularly problematic with respect to algal growth and therefore is treated with more copper than other parts of the reservoir.

Nicasio Reservoir was monitored in conjunction with three separate applications of copper sulfate as applied by the MMWD on June 19, August 9, and August 18, 2003. Water chemistry and toxicity were sampled at each event at different post application intervals in order to establish a dose-response curve relating water toxicity to copper application concentrations. On June 19, water was sampled before and immediately post application. Copper was applied again on August 8th and sampling took place 24 hours and 7 days post application. Experimental concentrations and risk quotients are summarized in **Tables 18 and 19**.

Table 18. 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[a]	0.0381 mg/l	0.0076 mg/l
0.068 mg/l	*C. dubia* EC50	**0.96**	**0.56**	**0.11**
0.03 mg/l	Daphnid NOEC	**2.18**	**1.27**	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

[a] It is known that sampling error led to the incorrect chemical characterization of the peak copper concentration of the Nicasio copper sulfate treatment.

Table 19. Porewater and Sediment Peak Concentration Risk Quotient Calculations for Chelated Copper Sulfate Applications (Reservoir Systems)

Experimental Concentration Range	**Toxicity Value**	**Toxicity measurement or guidance value**	**Risk Quotients**
Porewater			
2.31 mg/l	0.035 mg/l	*H. azteca* LC50	66[a]
Sediment			
1800 mg/kg	ERL 34 mg/kg	ERL NOAA SQC	53 [a]
	ERM 270 mg/kg	ERM NOAA SQC	6.6 [a]

[a] There are no LOCs for porewater concentrations. Sediment guideline values are intended for screening-level hazard comparison only (NOAA, 1999)
[b] Sediment guideline value intended for screening-level hazard comparison (NOAA, 1999)

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 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, although no increase in copper was measured. This is likely due to sampling error at a Nicasio reservoir application as the chemical characterization samples were collected prior to accurately locating the copper plume behind the application boat. By the time the toxicity samples were collected, the copper had sufficiently mixed and diffused, so it was not possible to accurately sample the plume. Peak water copper concentrations for the samples collected exceeded the LOC for daphnids, but not trout. 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.

Reduced growth of the amphipod *H. azteca* in sediments was found in samples from all stations. Samples from stations B01 and B02 significantly inhibited growth and survival. The highest copper concentrations occurred in sediment from these two stations. Copper concentrations reported at these two stations exceed sediment quality guidelines (Table 18) and concentrations at other stations approached those guidelines.

Sediment toxicity was observed in both the pre and post-application samples and had no clear relationship to copper applications. The porewater copper concentrations generally increased after application although the overall concentrations were lower than the 10-day LC50 for *H. azteca*. Overall sediment concentrations of copper did not increase from their already elevated levels.

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. PVID applied Cutrine Plus which is a copper ethanolamine mixture. SID applied Clearigate which is a copper ethanolamine mixture in an emulsified formulation. Both products contain unique

unspecified 'inert ingredients' that may cause them to have different environmental fates and toxicological properties.

Copper carbonate is the other major chelated copper product active ingredient. No monitoring of copper carbonate products was conducted.

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 or other structure to aid in mixing. Each treatment lasted for a few hours. In one application at Solano Irrigation District's Byrnes Canal and the only Potter Valley Irrigation District application monitored, toxicity to *C. dubia* and juvenile *O. mykiss* was observed in the preapplication samples and in the copper treated samples. At the second copper application at Byrnes Canal, no mortality was observed pre-application, but significant *C. dubia* and juvenile *O. Mykiss* mortality was observed after treatment began. The peak water concentrations detected during the three applications exceed the LOCs. Experimental concentrations and risk quotients are summarized in **Tables 20 and 21**.

Sediment toxicity was also observed in both systems. However, the porewater and sediment concentrations did not change significantly following the copper applications. The toxicity could be due to the levels of copper already present in the sediment, but TIEs were not performed to confirm this.

Table 20. 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 *Alonella* LC50	**0.144**	0.01	0.002
0.0023mg/l	Fathead Minnow larvae 48hr LC50	**621**	**43**	**7.39**

Table 21. Porewater and Sediment Peak Concentration Risk Quotient Calculations for Chelated Copper Applications (Irrigation Canal Systems)

Experimental Concentration Range	Toxicity Value	Toxicity measurement or guidance value	Risk Quotients
Porewater			
0.161 mg/l	0.035 mg/l	*H. azteca* LC50	4.6[a]
Sediment			Peak conc. (897 mg/l)
897 mg/kg	34 mg/l	ERL NOAA SQC	26.38[a]
	270 mg/l	ERM NOAA SQC	3.32[a]

[a] There are no LOCs for porewater concentrations. Sediment guideline values are intended for screening-level hazard comparison only (NOAA, 1999)

Conclusion

Copper was monitored for in several water bodies in both lake and canal systems. In both lakes studies, the dissolved copper was sufficient to have caused toxicity to juvenile *O. mykiss* for at least 24 hours after application, and toxicity in *C. dubia* for at least a week after application. In one canal system treated with chelated copper, the treated water was toxic to both juvenile *O. mykiss* and *C. dubia* while treatment was occurring, but dissipated quickly. The copper concentrations during application did exceed acute and chronic LOCs for *C. dubia* and Rainbow trout.

Mortality and inhibition of amphipod growth was observed in the reservoir treated with granular copper for benthic algae control. Sediment copper concentrations were far in excess of sediment quality guidelines and porewater risk quotients far above the chronic LOC for *H. azteca*, but the relatively high *H. azteca* survival rates suggest copper was not bioavailable in the majority of these samples. In a canal system, sediment toxicity was observed two weeks post application, however, chemical characterization did not confirm elevated copper concentrations and no TIE was conducted to provide confirmation.

The exceedances of the LOCs and sediment quality guidelines indicate that further risk characterizations of copper applications are appropriate. This work should be tailored to the type of system where applications are occurring (i.e. lentic vs. lotic systems).

Diquat Dibromide

Diquat dibromide was sampled at two locations during the 2003 sampling season. One location was the Sand Bay Isle Homeowners Association property where diquat was applied in March 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 monitored during both sampling events. Limited sediment monitoring because diquat adsorbs irreversibly to sediment and once bound is no longer considered bioavailable. Sediment chemistry was measured to complement the benthic bioassessment data. Additionally, sediment diquat concentrations were determined and sediment toxicity testing performed on 7-Mile Slough sediments in order to match the sampling protocol performed by DBW at this site for data comparison purposes. Sand Bay Isle also received a copper treatment later in the season.

Water chemistry and toxicity results are shown in Appendix D. Sampling was conducted according to the matrix shown in Appendix A. 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). Sand Bay Isle was not sampled 24 hours after application. Peak water diquat dibromide concentration risk quotients exceeded LOCs. Experimental concentrations and risk quotients are summarized for diquat in **Table 20** and for R-11 surfactant in **Table 21.**. Although surfactant was not applied with the diquat in these two cases, the nonylphenoloxylate concentration in the water in 7-mile slough 24 hours after application (69.7 ppb) exceeded the NOEC for Delta smelt.

Table 22. 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	*S. capricornutum*. EC50 (growth)	$RQ_{7\text{-Mile}}$=0.73 $RQ_{\text{Sand Bay}}$=0.04	$RQ_{7\text{-Mile}}$=9 $RQ_{\text{Sand Bay}}$=21	$RQ_{7\text{-Mile}}$=0.24
44 µg/l	Algae NOEC (biomass growth)	$RQ_{7\text{-Mile}}$=0.31 $RQ_{\text{Sand Bay}}$=0.02	**$RQ_{7\text{-Mile}}$=4** **$RQ_{\text{Sand Bay}}$=9**	$RQ_{7\text{-Mile}}$=0.1
32 µg/l	D. magna LC50	$RQ_{7\text{-Mile}}$=**0.43** $RQ_{\text{Sand Bay}}$=0.025	$RQ_{7\text{-Mile}}$=**5.6** $RQ_{\text{Sand Bay}}$=**13**	**$RQ_{7\text{-Mile}}$=0.14**
36 µg/l	Daphnid NOEC	$RQ_{7\text{-Mile}}$=0.38 $RQ_{\text{Sand Bay}}$=0.02	**$RQ_{7\text{-Mile}}$=5** **$RQ_{\text{Sand Bay}}$=11**	$RQ_{7\text{-Mile}}$=0.125
120 µg/l	Minnow NOEC	$RQ_{7\text{-Mile}}$=0.115 $RQ_{\text{Sand Bay}}$=6E-3	**$RQ_{7\text{-Mile}}$=1.5** **$RQ_{\text{Sand Bay}}$=3.3**	$RQ_{7\text{-Mile}}$=0.038
7600 µg/l	P. promelas LC50	$RQ_{7\text{-Mile}}$=0.0018 $RQ_{\text{Sand Bay}}$=1E-4	$RQ_{7\text{-Mile}}$=0.02 $RQ_{\text{Sand Bay}}$=0.05	$RQ_{7\text{-Mile}}$=6E-4
11 µg/l	Duckweed LOEC	**$RQ_{7\text{-Mile}}$=1.25** $RQ_{\text{Sand Bay}}$=0.72	**$RQ_{7\text{-Mile}}$=16** **$RQ_{\text{Sand Bay}}$=36**	$RQ_{7\text{-Mile}}$=0.4
18 µg/l	Duckweed EC50	**$RQ_{7\text{-Mile}}$=0.76** $RQ_{\text{Sand Bay}}$=0.044	**$RQ_{7\text{-Mile}}$=10** **$RQ_{\text{Sand Bay}}$=22**	**$RQ_{7\text{-Mile}}$=0.25**

Table 23. Porewater Peak Concentration Risk Quotient Calculation Diquat Dibromide Application

Experimental Concentration Range	Toxicity Value	Toxicity measurement or guidance value	Risk Quotients
Porewater			
7-Mile 90-195 µg/l	12-64 µg/l	*H. azteca* LC50	$RQ_{7\text{-Mile}}$= 16.25

[a] There are no LOCs for porewater concentrations.

Table 24. Risk Quotient Calculations for Surfactant (R-11) during Diquat Application in 7-Mile slough.

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.
		25.4 µg/l	<Reporting Limit	69.7 µg/l
5700 µg/l	*C. dubia* LC50	0.004	0	0.012
420 µg/l	*C. dubia* NOEC	0.060	0	0.16
1100 µg/l	*P. promelas* LC50	0.023	0	0.06
340 µg/l	*P. promelas* NOEC	0.075	0	0.21
700 µg/l	Delta smelt LC50	0.036	0	0.01
100 µg/l	Delta smelt NOEC	0.254	0	0.70
3900 µg/l	Sacramento splittail LC50	0.006	0	0.018
1900 µg/l	Sacramento splittail NOEC	0.013	0	0.037

Note: No surfactant was added to the tank mix during this application

Toxicity was observed in the acute and chronic *C. dubia*, and *S. capricornutum* tests in the sample collected from Sand Bay Isle after application. 100% mortality was observed in the two *C. dubia* tests. However, no toxicity was observed in water samples collected from 7-Mile slough. Sediment toxicity was observed in both 28-day *H. azteca* tests performed on 7-Mile Slough sediment. It is not clear if this was a direct effect of the diquat application because diquat is thought to be unavailable once it is bound to sediment. Additionally, 7-Mile Slough receives input from many sources including significant runoff from surrounding agricultural lands.

Conclusion

Diquat was sampled at two locations (one small pond and one delta slough). In the pond location, water toxicity was seen immediately following application. No toxicity was seen in the delta slough that could be attributed to directly to the diquat application. The diquat risk quotients calculated exceeded acute and chronic LOCs for both aquatic plants and animals. These exceedances indicated the need for more detailed risk characterization. In addition, surfactant concentration exceeded the Acute Endangered

LOC for Delta smelt and there were several LOC exceedances fro diquat from background diquat levels.

Fluridone

Fluridone was monitored at two locations in 2003. One location was Big Bear Lake, which was treated with pelleted fluridone for milfoil control. Half of the lake milfoil habitat was treated in 2002 and half in 2003. The second location was Costa Ponds, which is a fishing resort near Porterville. Costa Ponds is treated with liquid fluridone by California Department of Food and Agriculture. The ponds are treated with a backpack sprayer used from a small boat. Both pellet and liquid products are Sonar formulations.

Water and sediment chemistry and toxicity were monitored and the results shown in Appendix E. Epiphytic and benthic macroinvertebrate communities were sampled to determine non-target biota impacts. Samples were collected according to the sample matrices (Appendix A). Costa Ponds was sampled pre-application, two weeks post application and then again six weeks after application. Big Bear Lake was sampled two weeks after application because of logistical issues. An untreated site in the lake was used as a reference location.

In Costa Ponds, the fluridone water concentration ranged from 0.05 ppb before application to 7.2 ppb one hour after application. The porewater fluridone concentration ranged from 0.08-1.24 ppb. Toxicity was observed in all *S. capricornutum* tests conducted, including the water collected preapplication. This indicates that fluridone was not the cause of toxicity. No toxicity was observed in the *C. dubia* or *P. promelas* tests.

Risk quotients calculated from Merced Irrigation District water fluridone concentrations from the in early 2003 did exceed the Stonewort LOC. Experimental concentrations and risk quotients are summarized in **Table 25**.

In Big Bear Lake, the fluridone sediment concentrations ranged from 5.88-300 ppb. Mortality and growth inhibition was exhibited in the *H azteca* tests (10 and 28 day tests), but bore no relation to sediment fluridone concentration. The sediment fluridone concentration was also not correlated to the porewater fluridone concentration. Clear

Lake sediment and porewater concentrations (which had the highest fluridone concentrations) are shown in **Table 26**.

A special *Typha ssp* seed germination and plant growth toxicity test was performed. Both the mean root and shoot growth was impressed in sediments treated with fluridone. This indicates the need for further nontarget plant evaluations in fluridone treated systems.

Monitoring of a liquid fluridone application during the Phase 1 sampling season that was not completed in time for the Phase 1 report, found fluridone accumulation in the tissue of fish and crayfish two weeks after application. At four weeks after the cessation of treatment, tissue concentrations had returned to preapplication levels.

Table 25. 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)		
		Preapplication concentration	**Mid Application**	**Post Application**
		Non Detect	37 µg/l	102 µg/l
2.1 mg/l	*D. magna* LC50	0	0.018	0.048
200 µg/l	*D. magna* NOEC	0	0.185	0.51
6.2 mg/l	*P. promelas* LC50	0	0.006	0.016
1.88 mg/l	*P. promelas* NOEC	0	0.02	0.054
1.28 mg/l	Delta smelt NOEC	0	0.029	0.08
20 µg/l	Stonewort EC50	0	**1.85**	**5.1**

Table 26. Porewater and Sediment Peak Concentration Risk Quotient Calculations for Fluridone Applications in Clear Lake

Peak Conc.	Toxicity Value	Toxicity measurement or guidance value	Risk Quotients
Porewater			
31.2 µg/l	6.8 mg/l	Oyster embryo EC50	0.0045
Sediment			
ND-1625 µg/kg			

Conclusion

Fluridone was sampled at several locations. At the Costa Ponds site (a liquid and pelleted fluridone application site), toxicity to *S. capricornutum* before and after application was observed and therefore not clearly correlated with the fluridone concentration. Sediment toxicity was seen in Big Bear Lake (pelleted fluridone application), but could not definitively be related to the fluridone application.

A concern with fluridone is impact on non-target vegetation. The risk quotient calculated for Stonewort and the results of the Typha toxicity tests indicated the need for possible further risk characterization.

Glyphosate

Glyphosate was monitored in three locations during 2003. One site was Doris Drain, an agriculture return flow canal, near Ventura. The second site was Merced Irrigation District's Atwater Canal. Glyphosate were also monitored at Stone Lake National Wildlife Refugee. All applications were made with a tank mix of glyphosate and nonionic nonylphenolethoxylate surfactant.

Water chemistry and toxicity were monitored and the results shown in Appendix F. Epiphytic and benthic macroinvertebrate communities were sampled to determine non-target biota impacts. Sediment quality characteristics were determined to aid in interpretation of benthic bioassessment data. Samples were collected according to the sample matrices (Appendix A).

At Doris Drain, the glyphosate concentration ranged from 13.6 ppb (pretreatment) to 1800 ppb (immediately after treatment). In the Atwater drain the concentrations were approximately 38 ppb after application. At Stone Lake NWR, the glyphosate range was 27.5-91.9 ppb. Isolated cases of toxicity were observed, but have no correlation with glyphosate applications. Peak water glyphosate concentration risk quotients exceeded LOCs for algae. Experimental concentrations and risk quotients for glyphosate are summarized in **Table 27** and for R-11 surfactant in **Table 28.**

Table 27. Glyphosate Risk Quotient Calculations for Doris Drain 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+3 hour conc.	t+5 hour conc.	t+24 hours conc.
		13.6 µg/l	1800 µg/l	370 µg/l	175 µg/l	92 µg/l
42 mg/l	*P. promelas* NOEC	3E-4	0.035	0.0088	0.004	0.002
50 mg/L	Daphnia NOEC	3E-4	0.036	0.0074	0.0035	0.002
7.2 mg/l	*S. capricornutum* EC50	0.002	**0.25**	0.051	0.024	0.013
770 µg/l	*S. capricornutum* NOEC	0.018	**2.3**	0.48	0.22	0.12

Table 28. 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	*C. dubia* LC50	0	0.021	0.003
420 µg/l	*C. dubia* NOEC	0	0.29	0.047
1100 µg/l	*P. promelas* LC50	0	**0.11**	0.018
340 µg/l	*P. promelas* NOEC	0	0.35	0.058
700 µg/l	Delta smelt LC50	0	**0.17**	0.028
100 µg/l	Delta smelt NOEC	0	**1.2**	0.196
3900 µg/l	Sacramento splittail LC50	0	0.031	0.005
1900 µg/l	Sacramento splittail NOEC	0	0.063	0.01

Conclusions

Glyphosate was monitored at several locations and at all locations it was applied with a nonylphenol surfactant. No toxicity was found to be associated with any glyphosate application.

The glyphosate risk quotients calculated indicate the potential for some effects on *S. capricornutum* and possible need for further risk characterization. The surfactant risk quotients showed LOC exceedances for *P. promelas* and Delta smelt and warrants further risk characterization.

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 APMP Phase 2. 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 was 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 had a short window of bioavailability after application. To attempt to conduct a test within the methoprene breakdown time frame, it was felt to be worthwhile to attempt *in-situ* exposures. The test method was modified from the EPA standard *H. azteca* test methodology by UC Davis Marine Pollution Studies Laboratory scientists.

Water chemistry and toxicity results are shown in Appendix G. 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 no clouds were present and the temperature was over 100F.

Methoprene was detected in all sediment (preapplication and reference site) porewater samples. 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 preapplication 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 exceeded LOCs. Experimental concentrations and risk quotients are summarized in **Table 25**.

Swanton's marsh is treated with methoprene approximately twice a month. The fact that methoprene was found pre-application indicates that it is persistent in the soil for at least several weeks. USEPA methoprene reregistration 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 (USEPA 1982).

Table 29. 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?
Water				
>RL	900 µg/l	*D. magna* LC50	0	No
	14 µg/l	Daphnid LOEC	0	No
	48 µg/l	*P. promelas* NOEC	0	No
Porewater				
22.6 µg/l	2 µg/l	*M. bahia* LOEC	11.3	NA[a]
	1250 µg/l	*H. azteca* LC50	0.018	NA[a]
Sediment				
125-2080 µg/kg				

[a.] There are no LOCs for sediment or porewater.

The *C. tentans* toxicity test results were inconclusive. Significant mortality was seen at the two treated sites pre-application and post application. Significant growth reduction was seen in the samples collected at all three sites pre and post 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 mortality seen. 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 could have died due to environmental conditions (anoxia) or lack of food in the 10-day exposures.

The inconclusiveness 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 is very shallow still waters. Such a water environment often leads to anaerobic water and sediment.

Conclusion

Monitoring for methoprene is challenging because the environments it is commonly applied in do not lend themselves to traditional water and sediment sampling and testing methods (i.e. extremely shallow water and highly anoxic sediments). *In situ*

toxicity tests were completed. Little mortality was observed after 96 hours, but the 100% mortality observed after 10-day exposures indicated a problem with the test environment regardless of the presence of methoprene. *C. tentans* toxicity tests were performed in the lab, but the results were inconclusive as the lethal and sublethal toxicity observed could not clearly be attributed to methoprene. The methoprene concentrations did not correlate with the observed toxicity. Future experiments will be designed to assess impacts of methoprene on growth of amphipods and chironomids. By conducting exposures when more surface water is present in the marsh, we hope to avoid the anoxic conditions that confounded the results of the experiments. The risk quotients calculated do not indicate the need for further risk characterization, although potential risk from sediment exposure is unknown.

Methoprene is persistent in sediments over a several week time period.. The second highest sediment concentration (1800 ppb) was found in the sediment at the reference site. This reference site does receive water from upstream wetlands that are treated with methoprene far upstream of our reference location.

Triclopyr

California Department of Food and Agriculture (CDFA) personnel applied Renovate® triclopyr triethylamine salt at Bear Creek on July 23, 2003. This application was conducted under an experimental-use permit, as triclopyr was currently undergoing California Department of Pesticide Regulation registration. A one percent triclopyr and 0.5 percent Target Prospreader 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.

Water chemistry and toxicity were monitored in conjunction with the application. Epiphytic macroinvertebrate communities were sampled to determine non-target biota impacts. 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 another means.

Samples were collected according to the sample matrix (Appendix A) at an upstream and downstream station. The creek was very slow moving, with less than 1cfs flow in the treated area. Pre-application samples and post-application samples from time zero were collected from one primrose patch. The samples collected at two hours and 24 hours after application were collected from a second primrose patch 30 feet downstream of the primrose first sampled.

Water chemistry and toxicity results are shown in Appendix H. Triclopyr concentrations increased over time, with concentrations present at time zero (7.5 ppb), peaking at 250 ppb after two hours, and decreasing to 12 ppb at 24 hours post application. CDFA collected samples seven and twenty-one days after application and reported that no triclopyr was detected. There were no triclopyr risk quotient LOC exceedances. Experimental concentrations and risk quotients are summarized in **Table 30** and for TPA in **Table 31**.

Table 30. Peak Concentration Risk Quotient Calculations for Triclopyr Application

Peak Conc.	Toxicity Value	Risk Quotient	Toxicity measurement, regulatory tolerance, action or guidance value	RQ exceeds LOC or other regulatory guideline?
250 µg/l	11,000 µg/l	0.023	*S. costatum* diatom EC 50	No
	1000 µg/l	0.25	*S. costatum* diatom NOEC	No
	132,900 µg/l	0.002	*D. magna* Water Flea EC50	No
	110,000 µg/l	0.002	*D. magna* Water Flea MATC	No
	279,000 µg/l	0.0009	*P. promelas* Minnow LC50	No
	91,000 µg/l	0.003	*P. promelas* Minnow MATC	No

Table 31. 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	*C. dubia* LC50	**0.1**	0	0.032	**0.42**
420 µg/l	*C. dubia* NOEC	**1.36**	0	0.44	**5.7**
1100 µg/l	*P. promelas* LC50	**0.52**	0	**0.17**	**2.17**
340 µg/l	*P. promelas* NOEC	**1.68**	0	0.54	**7.03**
700 µg/l	Delta smelt LC50[a]	**0.81**	0	**0.26**	**3.41**
100 µg/l	Delta smelt NOEC [a]	**5.7**	0	**1.85**	**23.9**
3900 µg/l	Sacramento splittail LC50 [a]	**0.15**	0	0.047	**0.61**
1900 µg/l	Sacramento splittail NOEC [a]	0.30	0	0.097	**1.26**

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

Nonylphenolethoxylate surfactant was found in the creek water both pre and post application. 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 pre and post application for a variety of aquatic animal species.

No water toxicity was observed in samples collected after this application. However sampling error rendered them inconclusive. More triclopyr sampling will be conducted in 2004. The preapplication samples were toxic to *S. capricornutum*, *C. dubia* and *P. promelas*. This toxicity could be due to upstream inputs, but TIEs were not performed, as the toxicity would not have been due to the triclopyr application. Bioassessment results and interpretation are currently being compiled and will be incorporated into the final analysis.

Conclusion

Only one site treated with triclopyr and a nonylphenol surfactant was monitored in 2003. Risk quotient calculations showed no LOC exceedances for triclopyr and multiple surfactant LOC exceedances. These exceedances indicate that further risk characterization should be carried out.

SPECIAL STUDIES

Modeling Results

The results of the modeling workgroup are included in a separate accompanying report (Wadley *et al.* 2003).

Pesticide/Surfactant Endocrine Disruption Study

Preliminary studies were conducted to evaluate the *in vivo* and *in vitro* estrogenic activity of four aquatic pesticides (diquat, 2,4-D, glyphosate, and triclopyr) with and without two different alkylphenolethoxylate containing surfactants (R-11 and Target Pro-Spreader Activator (TPA)). These preliminary studies were conducted under a "worst-case" application scenario exposure regime. For pesticides or surfactants where increased estrogenic activity was observed a full dilution series of tests will be conducted in 2004. Retail pesticide stock solutions were diluted, according to the labels, in a 1:2 and 1:4.5 volume/volume ratio for R-11 and TPA, respectively. Each pesticide/surfactant mix was then diluted to the maximum application rate allowed for each pesticide. Juvenile *O. mykiss* were exposed for one week and their plasma/serum vitellogenin (Vtg) measured. TPA and R-11 exposure alone caused a 12 and 23-fold increase, respectively, in Vtg expression relative to untreated controls (see **Figures 4** and **5**).

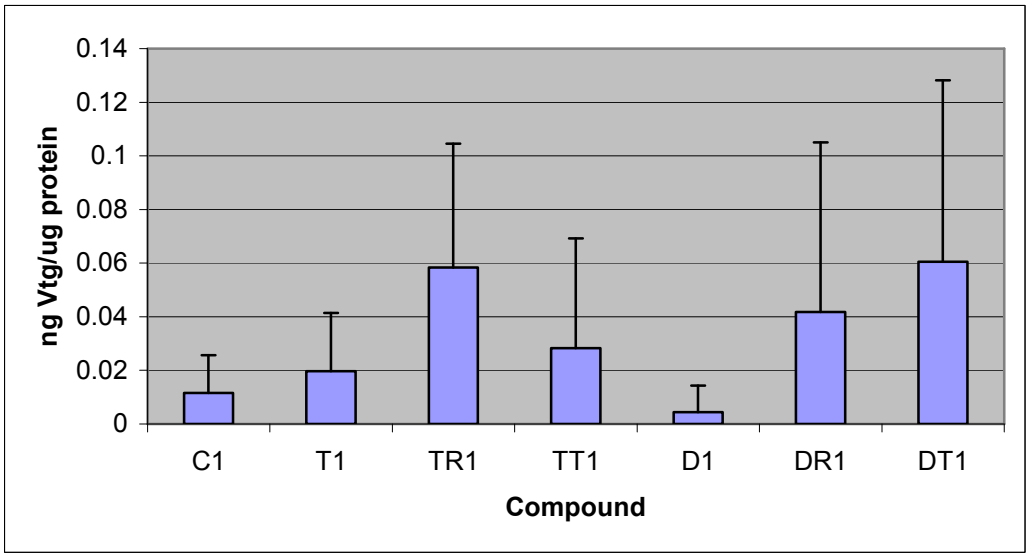
While glyphosate, diquat, and triclopyr were not estrogenic alone, 2,4-D caused a 4-fold increase in induction over animals exposed to untreated water. When R-11 was added to these herbicides, significant estrogenic activity was observed with glyphosate, triclopyr, and diquat, but no significant increases were observed with 2,4-D. With the exception of 2.4 D where estrogenic activity was reduced by R-11, Vtg expression was higher in animals exposed to the R-11/pesticide mixture than the pesticide alone.

Fish exposed to all TPA/pesticide combinations expressed greater Vtg than with pesticide alone. Unlike the R-11/2,4-D mixture, TPA/2,4-D caused significant increases in Vtg relative to controls, however, these values were not significantly different than 2,4-D without surfactant.

Based on these preliminary studies, 2,4-D, TPA, and R-11 can elicit estrogenic activity within Rainbow trout in a "worst-case" application scenario. Given the

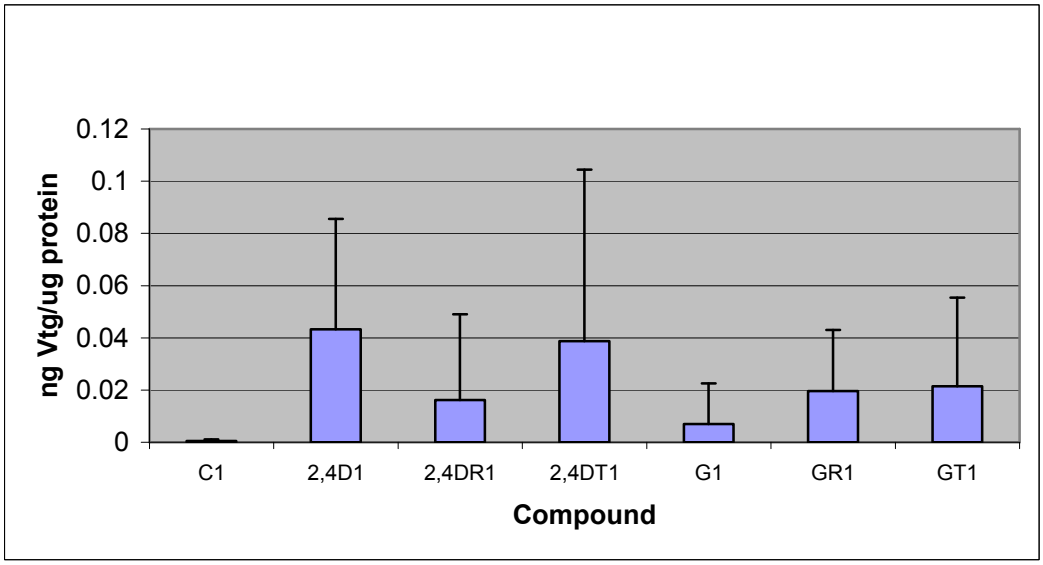
estrogenic response of the surfactants regardless of pesticide and the surprising estrogenic activity of 2,4-D, dose-response studies at environmentally relevant concentrations will be carried out with 2,4-D and each surfactant alone, and in combination with 2,4-D.

Figure 4. Effects of Nonylphenol-containing surfactants with triclopyr and diquat on vitellogenin production in Rainbow trout following aqueous exposure for 7 days.



Note: Each value represents the average of 5 individuals. C1 = control; T1 = Triclopyr (2.5 mg/L); TR1=Triclopyr + R11; TT1=Triclopyr + TPA; D1= Diquat (2 mg/L); DR1=Diquat + R11; DT1=Diquat plus TPA

Figure 5. Effects of Nonylphenol-containing surfactants with 2,4-D and glyphosate on vitellogenin production in Rainbow trout following aqueous exposure for 7 days.



Note: C1=control; 2.4D1= 2,4D (2 mg/L); 2,4DR1=2,4D+R11; 2,4DT1= 2,4D+TPA; G1=glyphosate (0.2 mg/L); GR1=glyphosate+R11; GT1=glyphosate+TPA

CONCLUSIONS

Use of the limited data gathered during the two pesticide application seasons that the APMP has existed should be limited to screening purposes only to identify where further risk characterization or research may be needed. APMP is not yet of sufficient spatial or temporal extent to directly inform regulatory change. Due to the limited time and budget of the project, no definitive conclusions can be drawn from the data accumulated to date. APMP generated chemical characterization, toxicity, and bioassessment data. The chemical characterization and toxicity data can be used for screening purposes. In complex field situations, bioassessments require multiple years of data before even preliminary conclusions can be drawn from them.

Specific conclusion concerning individual pesticides:

<u>2,4-D</u>

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 experiments indicate that 2,4-D may possibly cause endocrine disruptor at application rates in the laboratory.

The vitellogenin induction finding indicates the need for further study particularly under normal field conditions. This is a special study and not a routine monitoring recommendation.

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. 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 indicates that very high mortality to EPA water and sediment toxicity test species can be assumed. APMP could find no toxicological data on acrolein's principle breakdown product 3-hydroxypropanal.

Further refinement of the sampling methodology begun in 2003 is warranted as is investigation of 3-hydroxypropanal. It is recognized that residue values for this pesticide may be difficult to determine. Therefore, development of diagnostic response tests (i.e. phytomonitoring, sentinel bivalves and fish, etc.) should be explored.

Copper Sulfate

Copper sulfate applications were monitored in two reservoirs. In one reservoir treatment area treated with dissolved copper sulfate, toxicity (in the form of mortality) was observed for at least 24 hours after application in juvenile trout. Lethal (mortality) and sublethal (reproduction) toxicity was observed in Ceriodaphnia (water flea) up to one week after application. Peak concentration risk quotients showed acute and chronic U.S. EPA Office Pesticide Programs Levels-of-Concern (LOC) exceedances. At 24 hours post

application the risk quotients showed acute and chronic LOC exceedances. At one week post 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 treatment area. Follow up water sampling was not conducted and the reservoir received only one application in 2003. Mortality and growth inhibition was also observed in a number of the sediment samples. Sediment copper concentrations exceeded National Oceanographic and Atmospheric Administration (NOAA) Effect Ratio Low and Medium values. However, the limited toxicity 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 copper sulfate and each other in aquatic environments based on the chelating agent and other adjuvants.

In both systems where monitoring occurred, the water samples were almost uniformly toxic preapplication and post application. Therefore, no definitive conclusions can be drawn about the toxicity of mixed copper ethanolamines. Risk quotients showed some LOC exceedances depending on species sensitivity. 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.

Based on the lack of definitive data, 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. Risk quotients for *Selenastrum* indicate that immediately after application, when glyphosate concentrations are highest, Levels of Concern are exceeded. 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 may be warranted to further investigate a surfactant used in conjunction with the glyphosate.

Diquat Dibromide

Diquat dibromide was sampled at two locations (one small pond and one Delta slough). At both sites, 100% mortality was observed in the acute and chronic Ceriodaphnia toxicity tests one hour after application. Twenty-four hours after application to the Delta slough, no toxicity was observed in the treatment area. Additional samples were not gathered from the pond site. Risk quotients almost uniformly exceeded Levels of Concern at all sampling periods in the Delta slough (including preapplication) 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 in USEPA three species water or sediment amphipod toxicity tests. The peak concentration risk quotient for Stonewort did exceed an Acute LOC. Risk quotients for other species did not exceed LOCs. Fluridone was found to cause sublethal toxicity (decreased shoot and root length) to Typha. This would indicate a potential for impacts on nontarget plants.

Further risk characterization of impacts on nontarget 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 indicate 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 Bti.

Triclopyr

Triclopyr (in the triclopyr, triethylamine salt formulation) was monitored at one application only. Due to sampling error, the toxicity tests were rendered inconclusive and therefore no conclusions can be drawn as to the toxicity of triclopyr. Triclopyr peak concentration risk quotients show no LOC exceedances. Triclopyr is often applied with a surfactant which may have much higher toxicity than the active ingredient.

Limited further risk characterization is warranted to conduct toxicity testing. Risk characterizations may be warranted to further investigate a surfactant used with triclopyr.

Nonionic surfactants

The most commonly used surfactants at APMP monitoring sites were Target Prospreader Activator and R-11. Both are nonylphenolethoxylate surfactants. Peak concentration risk quotients indicate exceedances of LOCs for a wide range of animal species including Delta Smelt and Sacramento Splittail. Vitellogenin induction experiments in Rainbow trout indicate 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. There is only limited data available on 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 during Phase 2.

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 have 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.

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?* The Phase 2 monitoring approach began to address this issue through the tiered approach to monitoring in increasingly complex water bodies.

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 in Phase 2 addressed this question. In Phase 3 this will be looked at more closely.

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.

PHASE 3 (2004) PROPOSED SAMPLING PLAN

In Phase 3, SFEI will conduct a third year of monitoring to determine potential effects of aquatic pesticides on the environment. Non-chemical alternative project funds will be used to conduct further demonstration projects and continue the cost effectiveness evaluations. Phase 3 (2004) plans will not be finalized until after the meeting of the APMP SAC in March of 2004.

APMP Monitoring Program

Conducting a third year of monitoring will allow the APMP to pursue studies that would look at potential longer term effects of aquatic pesticide applications and conduct special studies already identified that could not be conducted due to time limitations. All studies will continue to be guided by the tiered monitoring approach developed for the first two years of the APMP and by the same Science Advisory Committee.

SFEI will continue to work through the tiered approached already developed. Tier 1 and 2 studies will be continued in certain cases. The studies that would be implemented during the third year are developed directly from the findings of years 1 and 2 as well as the guidance of SAC. The number of sites studied will decrease, but the amount of effort expended at each site will increase.

The studies that SFEI could implement during a third year of the APMP are:

1. Additional triclopyr sites would be studied using Phase 1 and 2 methods. One site is being studied this year, but since triclopyr use is currently allowed only under a research permit usage is currently very limited. This is likely to change in the next year or two after triclopyr receives its' California registration label.

2. Bioassessment studies would be conducted at selected 2003 sites for a second year. The focus would shift to looking at potential effects seen over a longer time scale and cumulative effects from multiple pesticide applications rather than effects of a specific pesticide application.

3. Additional mosquito vector control compounds could be studied using Phase 1 and 2 methods and/or special studies.

4. Fish and bivalve tissue studies would be conducted where human health action levels or benchmarks can be identified.
5. Modeling studies would be refined and expanded.
6. Studies on potential impacts on non-target macrophytes would be implemented. These were suggested at the February 2003 SAC meeting, but practical implementation could not be accomplished in the 2003 monitoring season.
7. Work on surfactants will be continued.

APMP Aquatic Pesticide Alternatives Project

During the second year of the nonchemical alternatives project, SFEI proposes to:

1. Work with subcontractors to develop scientifically rigorous evaluations of the impacts of additional non chemical pest control demonstration projects. Some of these demonstration projects could not take place in 2003 due to timing or logistical issues.
2. Continue development of the cost effectiveness evaluations of non chemical alternatives.

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APPENDICES