Aquatic Pesticide Monitoring Program

Phase 1 (2002) 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 to conduct two years of research and monitoring to: 1) provide the state with information to develop an acceptable general NPDES permit when the current emergency permit expires in order to effectively regulate discharges of aquatic pesticides to surface waters and, 2) explore non-chemical aquatic pest control alternatives. The specific APMP management objectives include:

1. Implement and integrate environmental monitoring and special 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.

To guide the development of the monitoring effort, a series of 'big-picture' questions (Management Questions) and second tier topic specific questions (Assessment Questions) were developed. Management questions developed are:

1. Which aquatic pesticides used in California have the highest "risk" of impacts to people and the environment?
2. What are the concentrations of the target aquatic pesticides in the environment (water, sediment, and biota) adjacent to their application point?
3. Are the measured concentrations above existing effects thresholds?
4. Which locations have the highest "risk" of beneficial use impairment?

5. What is the degree of biological impacts to non-target biota from application and exposure to aquatic pesticides?

6. What Best Management Practices are currently being used to mitigate potential impacts from aquatic pesticide application?

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

Per the suggestion of the TRG, a tiered monitoring approach was implemented to help the program focus its resources appropriately. The three tiers are 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 "basic" monitoring 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 assess aquatic biota impacts.

Tier 3. Utilize special studies, bioassessments, California listed species, and sublethal effects to more fully characterize aquatic pesticide environmental impacts where accumulation or effects are found or literature indicates may be found. Use monitoring data to calibrate and refine models that will allow the application of APMP findings to other unmonitored sites.

The TRG also suggested focusing on the aquatic pesticides acrolein, fluridone, and copper sulfate due to their wide use and high profile during the first program year. Glyphosate was added to this list because of its widespread use. Additional pesticides

that may be added during the second year of the program are 2,4-D, diquat dibromide, endothal, triclopyr, and methoprene.

Sampling was conducted between August 2002 and February 2003, and was coordinated with individual organizations applying selected pesticides in different settings: Merced Irrigation District's (MID) application of acrolein to control submerged macrophytes in irrigation canals; Orange County Public Works Department's application of glyphosate to control emerged aquatic weeds in storm water control canals and canal banks; Marin Municipal Water District's (MMWD) application of copper for control of floating and benthic algal in reservoirs; Lake County Agriculture Office's application of fluridone in pellet form to control an introduced aquatic weed (Hydrilla) in Clear Lake; and MID's application of liquid fluridone to control macrophytes in their main irrigation canal. These sites were selected in order to sample in a selection of water body types, pesticide user groups, and geographic distribution. The chemistry and toxicology workgroups devised sampling plans appropriate to each water body and pesticide chemical characteristics. During this first year only Tier 1 and 2 monitoring techniques were utilized. This included water, porewater, and sediment chemical analysis and matrix quality parameters, tissue collection and analysis, and water and sediment toxicity testing. Tier 3 techniques will be implemented during year 2 of the program.

The results of the work conducting during year one of the APMP, while beginning to provide data on aquatic pesticide behavior in the environment, also allowed SFEI the opportunity to test and refine monitoring methods and sampling techniques. The data from MID's acrolein application site indicates that sampling techniques need to be refined in order to be able to collect samples that will provide reliable data. In addition, further investigation of the Baker Testkit (a field colorimeter designed for acrolein detection) is also warranted as this may prove to be the most efficient method for analysis of environmental samples.

The glyphosate sampling in Orange County highlighted the difficulty of sampling in urban streams that receive uncontrolled inputs of water. Uncontrolled inputs make it difficult to ascribe any effects seen in the toxicity testing to the aquatic herbicide application. Also, the surfactants used with herbicide applications need to be more

thoroughly investigated as there is the potential for them to be toxic to aquatic animal life.

The copper sampling in MMWD's reservoirs indicated little toxicity in the system despite high copper concentrations in several of the samples. This indicates that a second year of toxicity and chemical analysis data should be gathered to confirm the results of the first year and bioassessments be performed to further enhance the monitoring techniques.

The fluridone sampling in Clear Lake again indicated little toxicity in the samples collected. More data should be gathered to confirm these results and bioassessments performed to enhance the monitoring efforts.

The fluridone sampling data from MID's main canal points to the need for further investigation. Fluridone was found to be present in trace amounts in several sediment and rainbow trout tissue samples collected prior to the treatment. However, the origin of the fluridone in the preapplication samples could not be definitively established. Concentrations increased in the samples taken two weeks after application in both sediment and tissue. Five weeks after application tissue samples were again collected and no fluridone was found to be present.

During its second year, the APMP will be expanding the number of sites investigated for each of the above pesticides as well as the number of pesticides investigated. In addition, a greater variety of sampling techniques will be employed at each site.

Aquatic Pesticide Monitoring Program
Phase 1 (2002) Project Report

INTRODUCTION

Background

This is the Phase 1 (2002) project report of the Aquatic Pesticide Monitoring Program (APMP). This report covers the organization of APMP and its development as a statewide environmental monitoring program. The results of Phase 1 (2002) monitoring are included, along with the proposed work plan for the Phase 2 (2003) monitoring effort.

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.

Management Objectives

The purpose of the APMP is to provide information to the SWRCB and the Regional Water Quality Control Boards to enable them to effectively regulate discharges of aquatic pesticides to surface waters. The APMP management objectives include:

1. Implement and integrate environmental monitoring and special 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.

To help guide the development of the monitoring effort, Management and Assessment questions were developed at the beginning of the program. 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, which were 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.
- Pilot projects for promising alternatives may be conducted and monitored to evaluate non-toxic or less-toxic pest control methods that may provide a practicable substitute for pesticide application.

The non-chemical aquatic pest control portion of the APMP is to determine the feasibility of such non-chemical alternatives to chemical control in California waters. The focus will be rigorous, scientifically defensible assessments of projects in California waters already underway or pilot projects planned and executed by SFEI staff. These projects will be conducted under natural conditions and, where possible, in parallel to similar water bodies treated with chemical pesticides.

The usefulness of non-chemical approaches in various conditions will be determined by quantitatively comparing their economic and environmental impacts. To determine economic feasibility, cost benefit analyses will be conducted for chemical versus non-chemical alternatives. Environmental factors for study will be selected based on current knowledge gaps and regulatory concerns. Potential research areas include: 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 method spreads invasive species. For each site and method, the factors to be compared will depend on local information needs and the feasibility at that particular site. The ultimate goal of the non-chemical alternatives project will be to produce a management tool, in the form of a report, that individuals needing to control aquatic pests can turn to identify which non-chemical methods would be most appropriate for their particular situation.

Organization

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

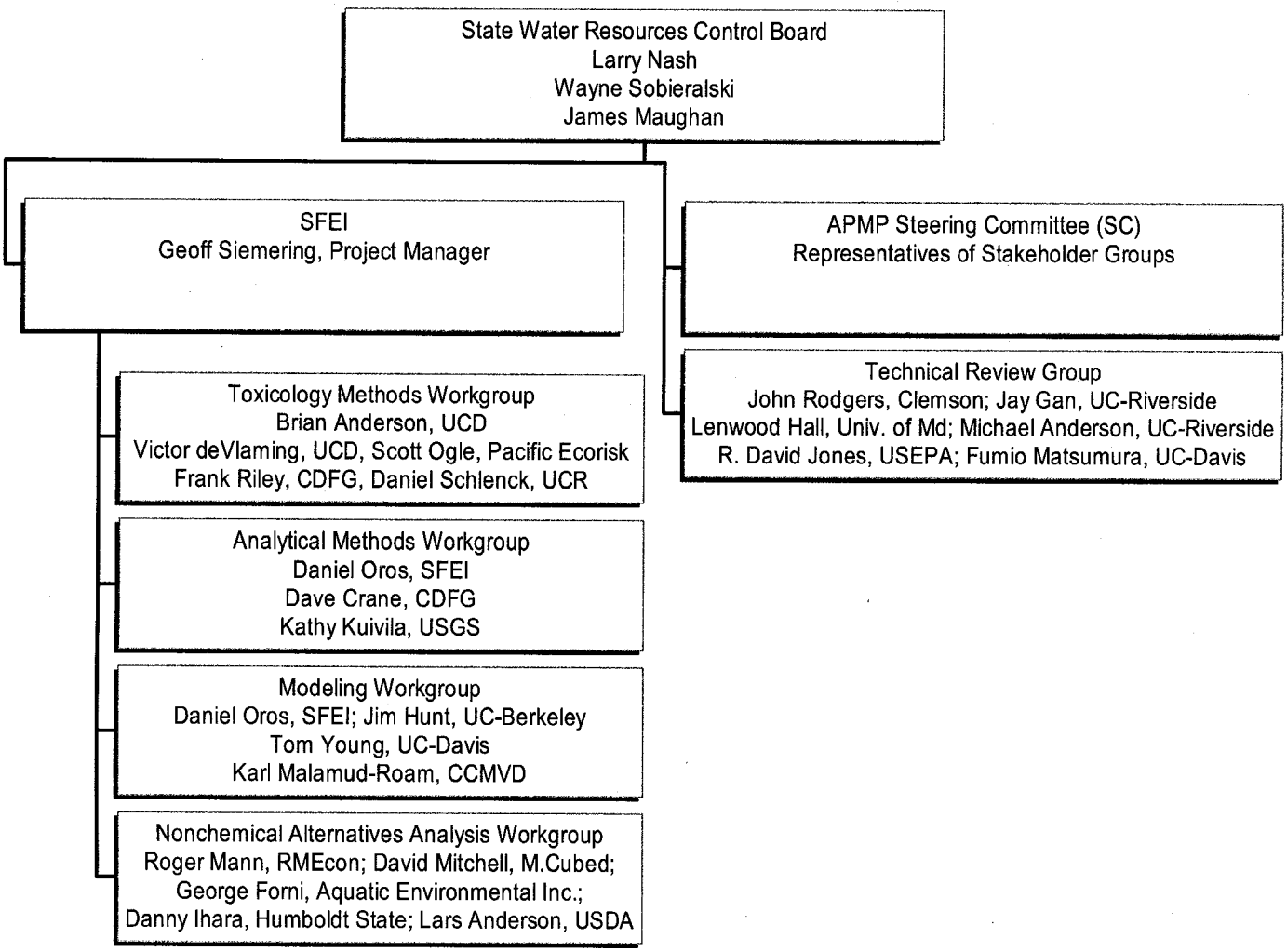

Figure 1. APMP Organizational Structure

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. Initial 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 for the remainder of the year. Quarterly meetings will continue through Phase 2 (2003) of the APMP. Steering committee members and alternates are listed in **Table 1**.

Table 1. Steering Committee Member List

First Name	Last Name	Company	Address	City, State	Zip Code	Phone Number	E-Mail Address
Emily	Alejandrino	RWQCB V	3442 Routier Road, Suite A	Sacramento, CA	95827	916 255 0736	alejane@rb5s.swrcb.ca.gov
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Bill	Taylor	Metropolitan Water District of S. Calif.	700 Moreno Ave	La Verne, CA	91750	909 392-5149	wtaylor@mwdh2o.com
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Technical Review Group

The Technical Review Group (TRG) is composed of six 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 three times: once to review the Phase 1 (2002) draft monitoring plans, once to review the

results and interpretations of the Phase 1 (2002) monitoring effort and plans for the Phase 2 (2003) monitoring effort, and once to review the final APMP monitoring results. The TRG members are consulted periodically as technical questions arise. TRG members are listed in **Table 2**.

Table 2. Technical Review Group Members

John H. Rodgers, Ph.D.	Clemson University Institute of Environmental Toxicology 509 Westinghouse Road Pendleton, SC 29670 jrodger@clemson.edu
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Chemistry Workgroup

The Chemistry Workgroup was established to identify and develop the laboratory methodology necessary to implement the aquatic pesticide sampling and monitoring program. The initial workgroup meetings focused on developing a work plan and identifying and prioritizing, from the Steering Committee's list of priority aquatic pesticides, those pesticides for which analytical methods were readily available and for which methods may need further development. **Table 3** lists the members of the Chemistry Group.

Table 3. Chemistry Workgroup Members

Dave Crane, Ph.D.	CA Department of Fish and Game Fish and Wildlife Water Pollution Control Laboratory 2005 Nimbus Road Rancho Cordova, CA 95670 Tel. (916) 358-2859 dcrane@ospr.dfg.ca.gov
Kathy Kuivila, Ph.D.	U.S. Geological Survey, Placer Hall 6000 J Street Sacramento, CA 95819-2605 Tel. (916) 278-3054 Email: kkuivila@usgs.gov
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The workgroup also administered the following tasks during the Phase 1 (2002) monitoring effort:

Task 1. Literature review of existing analytical methods: A scientific literature review was conducted by SFEI and this information was provided to the Chemistry Workgroup. 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. Development and application of current-use analytical methods: The current-use analytical methods that are applied for determining aquatic pesticide levels and their degradation byproducts in water, sediment and tissue samples were evaluated. All or certain aspects of current-use analytical methods that met the needs of the APMP were incorporated into the monitoring effort where it was feasible. The methods that were used for analyzing the target pesticides are shown in **Table 4**.

Table 4. Chemical Methods Used for Pesticide Analysis.

Pesticide	Method of Analysis	Registrant/ Manufacturer
Acrolein	DNPH derivitization with HPLC-DAD (EPA Method 8315A modified)	Baker Petrolite, Houston, Texas
Copper (water)	Atomic Absorption, furnace technique.	Multiple registrants
Copper (sediment)	Atomic Absorption, flame and furnace techniques.	Multiple registrants
Copper (tissue)	Atomic Absorption, flame and furnace techniques.	Multiple registrants
Fluridone (water)	HPLC-DAD-Fluorescence or ELISA	SePRO Corporation, Carmel, Indiana
Fluridone (sediment)	Pressurized fluid extraction (PFE) with gel permeation chromatography cleanup followed by either HPLC-DAD-Fluorescence or HPLC-MS.	SePRO Corporation, Carmel, Indiana
Fluridone (tissue)	Pressurized fluid extraction (PFE) with gel permeation chromatography cleanup followed by either HPLC-DAD-Fluorescence or HPLC-MS.	SePRO Corporation, Carmel, Indiana
Glyphosate	EPA Method 547 Direct injection HPLC-Fluorescence with post column derivitization.	Monsanto (Aquamaster), St. Louis Missouri and Dow Agrochemicals (Rodeo), Indianapolis, Indiana
Diquat Dibromide (water)	C8 extraction, ion-pair HPLC separation with diode array (DAD) / fluorescence detection	Syngenta, Basel Switzerland
Diquat Dibromide (sediment/tissue))	Acid digestion, C8 extraction, ion-pair HPLC separation with diode array / fluorescence detection	Syngenta, Basel Switzerland
Endothal (water)	Ion Exchange Extraction, Acidic Methanol Methylation and GC/Mass Spectrometry Certified EPA method 548.1.	Elf Atofina Chemicals, Philadelphia, Pennsylvania
Methoprene	Use of manufacturer's proprietary method by CDFG	Zoecon Corporation, Dallas, Texas
2,4-D (water)	Liquid-Solid Extraction and GC with Electron Capture Detector	Multiple Registrants
2,4-D (sediment)	HPLC	Multiple Registrants
2,4-D (tissue)	HPLC	Multiple Registrants

Task 3. Validating current-use analytical methods: Analytical methods validation is a crucial step in the quality assurance (QA) program. This task included analysis of National Institute of Standards certified standard reference materials and matrix spikes for the determination of QA information (e.g., method detection limits, precision, accuracy, surrogate standard recovery, and calibration checks). This method validation was performed by the analytical laboratory contractor.

The workgroup identified the California Department of Fish and Game-Water Pollution Control Laboratory (CDFG–WPCL) as the primary contract laboratory

to conduct the chemical analysis of pesticides in APMP samples. In addition, some water samples were sent to SePRO for fluridone concentration analysis. The CDFG-WPCL has submitted the analytical methods standard operating procedures (SOPs), laboratory quality assurance and quality control (QA/QC) protocols, and validation study results to the APMP.

Task 4. Development of field sampling and handling procedures: Field sampling, sample storage, and sample handling protocols were developed by the workgroup in order to ensure the integrity of the samples for chemical testing.

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 used by selected public agencies for nuisance plant and animal control. **Table 5** lists the members of the toxicity workgroup.

Table 5. Toxicology Workgroup Members

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Daniel Schlenk, PhD	Dept of Environmental Sciences University of California-Riverside Riverside, CA 92521 Tel. (909) 787-2018 daniel.schlenk@ucr.edu
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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. Literature review of toxicity of pesticides: A scientific literature review was conducted by SFEI and this information was provided to the workgroup. 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. Identification and development of 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. In addition, 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.

Modeling Workgroup

The Modeling Workgroup was established 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 will provide recommendations on which surface water screening and assessment models will be used. The screening and assessment models that are evaluated will be incorporated into the monitoring program. The modeling information will contribute to the understanding of aquatic pesticide fate, transport, persistence, and exposure concentrations of pesticides in surface waters. The modeling efforts will help to identify areas where monitoring should occur. Once the pesticide data (water concentrations and distributions) have been collected, they will be used to calibrate models, if possible, for future use in designing discharger monitoring plans. The Modeling Workgroup was started in December 2002 and will accomplish its mission through the following tasks during the Phase 2 (2003) monitoring effort:

Task 1. Identify workgroup participants: Scientist and modelers from the public and private sectors were identified and asked to participate in the workgroup. **Table 6** lists the members of the modeling workgroup.

Table 6. Modeling Workgroup Members

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Task 2. Literature review of models and pesticides of concern: A literature review will be conducted by SFEI and the information will be submitted to the workgroup. The information will be 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). The literature review will also include information on pesticide application rates, degradation byproducts, pesticide mixtures and formulations, persistence, fate, transport pathways, partitioning behavior between aquatic matrices (water, sediment, tissue, and air), environmental occurrence, and toxicity.

Task 3. Evaluate and recommend appropriate assessment models: Screening and assessment models that are identified from the literature review will be evaluated. The models that meet the needs of the monitoring program will be incorporated into the monitoring effort where it is feasible.

Task 4. Conduct pilot modeling study: An applicable screening and assessment model will be identified and a pilot modeling study will be conducted. Phase 1 data will be used for its ability to calibrate and validate the model. Results of the pilot modeling will be used for making recommendations to the APMP (e.g., address the need to make changes or improvements in the sampling program to meet modeling needs, uses of modeling results, etc.)

Task 5. Information dissemination: A technical report will be produced and submitted to the APMP.

Nonchemical 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:

Task 1. Identify workgroup participants: Scientist and modelers from the public and private sectors were identified and asked to participate in the workgroup. **Table 7** lists the members of the modeling workgroup.

Table 7. Nonchemical Alternatives Workgroup Members

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Task 2. Conduct a literature review of nonchemical pest control alternatives and survey of nonchemical alternatives methods practitioners and researchers: Conduct a literature review of nonchemical alternatives, both those currently in commercial use and ones under development. From this literature review, methods will be identified that have a high potential for success in controlling aquatic pests in California where chemical pesticides are currently being used. Contacts will be made with companies, agencies, and organizations involved in nonchemical aquatic pest control. In addition, efforts will be 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 will also include a survey of permit and regulatory requirements for each nonchemical pest control scenario.

Task 3. Participate in the design and execution of demonstration projects: Design demonstration projects to test the effectiveness of the greatest number of nonchemical alternatives that the APMP budget will allow. These projects will be

conducted under real environmental conditions and in parallel to similar water bodies treated with chemical pesticides. Where possible, project funds will be leveraged by working in conjunction with nonchemical pest control projects that are already being conducted.

Task 4. Cost/effectiveness analysis: Conduct cost/effectiveness analyses of nonchemical 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.

Task 5. Information dissemination: Report details of demonstration projects and cost/benefit analyses to the SWRCB.

MONITORING PROGRAM

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.

The target aquatic pesticides and sampling sites that were selected for monitoring were based on the following criteria:

1. Recommendations from the TRG,
2. Availability of relatively static water bodies with limited, or well-characterized inputs,
3. Existence of chemical analysis methods with detection limits sufficient for ambient environmental monitoring,
4. Availability of application sites in Northern, Central, and Southern California,

5. Diversity of pesticide user groups (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), while Tier 3 will be conducted during Phase 2 (2003).

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

Tier 2. Conduct "basic" monitoring 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 assess aquatic biota impacts.

Tier 3. Utilize special studies, bioassessments, California listed species, and sublethal effects to more fully characterize aquatic pesticide environmental impacts where accumulation or effects are found or literature indicates may be found. These techniques would also be used to bridge data gaps in the existing science of the target aquatic pesticides.

The types of studies that can be reasonably conducted during Phase 1 and 2 include: spatial and temporal extensions of existing discharger monitoring plans, accumulation of pesticides in sediments (core, porewater, and suspended sediment analysis), and bioaccumulation of pesticides in aquatic biota. 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. Pesticide impacts or lack thereof during Phase 1 (2002) monitoring will guide the development of Phase 2 (2003) monitoring. Phase 2 (2003) will also include looking at potential subtle effects due to chronic exposure to pesticides (i.e. bioassessments and other special studies). Because it

is often easier to identify the need for special studies only after basic monitoring has already been conducted, all Tier 3 special studies will be designed and implemented during Phase 2 (2003). The goal of this work is to produce data that are specific to California's aquatic environments and species.

Potential target pesticides were ranked based on the following criteria: aquatic uses, amount used, common usage, toxicity/risk, public perception, reliable analytical methods, and regulatory significance. This 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 pesticides and their rankings are shown in **Table 8**. 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. The regulatory areas that were considered for sampling included irrigation supply systems, drinking water reservoirs, exotic weeds (canals and coastal), mosquito abatement, flood control, drainage, and storm water, and recreational impoundments (golf courses and parks).

Table 8. Pesticide Ranking Table

Chemical	Selec-tivity	Toxicology				Phys Chem			Perception	Total Score	**Final Ranking**
1 – low risk 5 – high risk		Indirect	Ecosys tem	Terres trial	Human	Half -life	Kow	Mobilit y		Sum of criteria scores	
Acrolein	5	4	5	2	(4)	1	1	5	5	32	**1**
Copper (total and ionic)	2	4	4 - 5	1 – 2	1	2[1]	2	2 – 3	5	26	**2**
Diquat dibromide	3	4	2 - 3	1	1	1	1	1	3	18	**5**
Endothal	2	4	2	1	(1)	2	(3)	(3)	2	19	**4**
Fluridone	3	2	1	1	1	3	2-3	3	1 – 2	19	**4**
Glyphosate	5	1	1	1	1	1	1	1	(4)	16	**6**
Triclopyr	1	4	2	1	(1)	2	(3)	(3)	3 – 4	19	**4**
2,4-D (salt)	1	(3)	2 - 3	1 – 2	1	2	3	2	3 – 4	20	**3**

[1]Bioavailable form
() estimated values
Note: All aquatic pesticides used primarily by Mosquito Vector Control Districts have been deferred until the next sampling cycle to allow for time to develop analytical methods and identify sampling sites.

Sampling Program

This first round of Phase 1 (2002) sampling was conducted between August 2002 and February 2003, and was coordinated with individual organizations applying selected pesticides in different settings: Merced Irrigation District's (MID) application of acrolein to control submerged macrophytes in irrigation canals; Orange County Public Works Department's application of glyphosate to control emerged aquatic weeds in storm water control canals and canal banks; Marin Municipal Water District's (MMWD) application of copper for control of floating and benthic algal in reservoirs; Lake County Agriculture Office's application of fluridone in pellet form to control an introduced aquatic weed (Hydrilla) in Clear Lake; and MID's application of liquid fluridone to control macrophytes in their main irrigation canal. Following recommendations from the APMP Toxicity and Chemistry Workgroups, SFEI developed a sampling plan for each study area. The sample matrices for each of these sampling events are presented in **Tables 9, 10a, 10b, 11, 12 and 13**. The exact field sampling dates were determined after consultation with individual aquatic pesticide applicators. All organizations listed above agreed to cooperate with the monitoring effort and notified the APMP manager when they were planning on applying the pesticides to their designated water bodies. The locations of the various water bodies are shown in **Figure 2**.

Table 9. Merced Irrigation District Acrolein Application

Pesticide in Use	acrolein
Approximate Use Pattern	Applied biweekly between June and August
Analyses Performed	Conventional water quality parameters, pesticide concentration
Water Samples Collected	
Time	**Location**
1)Pretreatment (t-0.5 hr)	At application point immediately below canal gate
2) t + 2hr	Two miles downstream of application point where uniform mixing was achieved
3) t + 72 hr	1) Inside bypass gate at bottom of canal at point where water could be returned to Merced River 2) Outside a second bypass gate at the end of a lateral canal

Table 10a. Marin Municipal Water District, West Marin Watershed

Waterbody	Soulajule Reservoir Nicasio Reservoir
Pesticide in Use	copper sulfate, dissolved
Approximate Use Pattern	Applied to Nicasio reservoir approximately every three weeks during May-August Soulajule is not treated for algal control
Analyses Performed (Water Sampling)	Conventional water quality parameters, acute and chronic Ceriodaphnia toxicity test, 96-hr larval rainbow trout toxicity test, Cu concentration
Analyses Performed (Sediment Sampling)	10-day Hyallela toxicity tests on all samples, 28-day Hyallela toxicity tests on two Soulajule samples and three Nicasio samples, sediment quality parameters, Cu concentration, Cu porewater concentration
Water Samples Collected	
Time	**Location**
Soulajule:	One sample for reference comparison
Nicasio:	None, MMWD stopped drawing from reservoir and discontinued treatment before sampling could occur
Sediment Samples Collected	
Time	**Location**
Soulajule:	One day following Nicasio sample collection, Six samples collected from randomly selected sites
Nicasio:	2.5 weeks after final application, Twelve samples collected from randomly selected sites

Table 10b. Marin Municipal Water District, Mount Tamalpais Watershed

Waterbody	Lake Lagunitas Reservoir Bon Tempe Reservoir
Pesticide in Use	copper sulfate, granular
Approximate Use Pattern	applied to Bon Tempe reservoir three times between June and August Lake Lagunitas is not treated for algal control
Analyses Performed	10-day Hyallela toxicity tests on all samples, 28-day Hyallela toxicity tests on two Bon Tempe samples and one Lake Lagunitas sample, sediment quality parameters, Cu concentration, Cu porewater concentration
Sediment Samples Collected	
Time	**Location**
Bon Tempe	2.5 weeks after final application, six samples collected from randomly selected sites
Lake Lagunitas	At time of Bon Tempe sample collection, two samples collected from randomly selected sites

Table 11 Lake County Agriculture Office Fluridone Treatment

Waterbody	Clear Lake
Pesticide in Use	fluridone, pellet form
Approximate Use Pattern	Applied to segments of near shore areas on rotating bases 3-4 times during summer months
Analyses Performed	10-day Hyallela toxicity tests on all samples, 28-day Hyallela toxicity tests on two treated samples and one untreated sample, sediment quality parameters pesticide concentration, pesticide porewater concentration
Sediment Samples Collected	
Time	**Location**
2.5 weeks after final application	Two samples collected from untreated sections and six samples collected from treated sections

Table 12 Merced Irrigation District Fluridone Application

Waterbody	Main Canal
Pesticide in Use	fluridone, liquid formulation
Approximate Use Pattern	Applied to canal every other year, treatment is eight weeks in length
Analyses Performed (Water Sampling)	Conventional water quality parameters, pesticide concentration
Analyses performed (sediment sampling)	Analyses performed 10-day Hyallela toxicity tests on all samples 28-day Hyallela toxicity tests on one sample Sediment quality parameters Pesticide concentration Pesticide porewater concentration
Analyses performed (tissue sampling)	Pesticide concentration
Water Samples Collected	
Time	**Location**
Pretreatment (t-2 days)	3 miles downstream of application point
Mid treatment period	3 miles downstream of application point
24 hours after treatment cessation	3 miles downstream of application point
Sediment Samples Collected	
Time	**Location**
Pretreatment (t-2 days)	Three random sites between 2 and 3 miles downstream of application point
Two weeks after treatment cessation	Three random sites between 2 and 3 miles downstream of application point
Tissue Samples Collected	
Time	**Location/ Species**
Pretreatment (t-2 days)	Crayfish, rainbow trout
Two weeks after treatment cessation	Crayfish, rainbow trout, Sacramento suckers
Five weeks after treatment cessation	Crayfish, rainbow trout, Sacramento suckers

Table 13 Orange County Pubic Works Department

Waterbody	Bolsa Chica Canal
Pesticide in us	glyphosate with nonionic surfactant
Approximate use pattern	Applied two to thee times between June and August
Analyses performed	Conventional water quality parameters, EPA 96-hour three species toxicity tests on all samples, chronic Ceriodaphnia test on all samples, pesticide concentration
Water Samples Collected	
Time	**Location**
1) Pretreatment (t-0.25 hr)	At downstream edge of treatment area
2) t = 0	At downstream edge of treatment area
3) t + 2.5 hr	At downstream edge of treatment area
4) t + 4.5 hr	At downstream edge of treatment area
5) t + 23 hr	At downstream edge of treatment area
6) t + 24 hr	2.5 miles downstream of treatment area

Figure 2. Phase 1 (2003) sampling locations.

For the Phase 1 (2002) monitoring effort, four water body types were sampled. The water body types that were sampled included irrigation canals, a storm water control canal, a lake, and drinking water reservoirs. Detailed methods for the collection, storage, and handling of APMP samples are included in the APMP 2002 Quality Assurance Plan (QAP).

The samples were collected at the following locations: 1) four reservoirs of the Marin Municipal Water District, 2) within two Merced Irrigation District canals, 3) in Orange County Public Works Department Bolsa Chica canal, and 3) in Clear Lake. Sampling events were closely coordinated with the monitoring programs of permit holders that applied the pesticides to these water bodies. The water and sediment samples that were collected were well distributed both spatially and temporally. All sampling was conducted by Pacific Ecorisk Laboratory (PER) staff and Applied Marine Science staff in conjunction with SFEI staff between July 20 and February 19, 2003. All aquatic pesticides in use at each site were applied according to both registration label instructions and the applicators individual monitoring plans.

Field Records

Upon arrival at each sampling station, the field scientists recorded global positioning system (GPS) coordinates (*e.g.,* latitude and longitude), weather conditions, station depth, and sample depth. Finally, project-specific labels were applied to appropriate pre-cleaned sample bottles following the sampling plans developed by SFEI. All the necessary site information and conventional water quality measurements are recorded in the appropriate Appendices. The original field log sheets are on file at SFEI.

Sediment Sampling and Analysis

Sediment samples were collected between two to three weeks after application of aquatic pesticide into specific water bodies (Marin Municipal Reservoirs, Clear Lake, and Merced Irrigation District Main Canal). The sediment quality parameters that were measured are listed in **Table 14**. The sampling procedure followed the methods described in the APMP Quality Assurance Plan (QAP). Briefly, all sediment samples were collected using "clean" techniques. Sediment samples for chemical analyses and toxicity assessments were collected by PER staff supported by one to two SFEI staff. A Van Veen grab (0.1 m^2 sample area) was deployed from a 21' boat using a winch with an electric motor for large water bodies or by hand for smaller areas. The top two cm of each sediment grab were removed from the Van Veen grab using a pre-cleaned stainless steel spoon, and the collected sediment were placed into a pre-cleaned stainless steel bowl. A minimum of two liters of sediment were collected from each station for use in chemical analysis and toxicity testing. The total volume of sediment collected varied according to

the exact sampling plan for each location. These "top two cm of sediment aliquots" from multiple grabs at each sampling station were then composited and homogenized by thoroughly mixing with a stainless steel spoon, and the resulting homogenized composite was placed into appropriately cleaned and pre-labeled high density polyethylene (HDPE) or glass containers. Sampling equipment was decontaminated with Alconox® solution, rinsed with de-ionized water, and rinsed with site water prior to use between sampling stations.

Table 14. Sediment Quality Parameters

Parameters	**units**
% gravel (> 2 millimeters)	% dry weight
% sand (2 mm > 62 µm)	% dry weight
% fines (< 62 µm)	% dry weight
Nitrate-Nitrogen	mg/kg
% solids	% dry weight
Total Nitrogen	mg/kg
Total Organic Carbon	mg/kg
Pore Water Pesticide Concentration	mg/l or µg/L
SEM-AVS (for copper treatments only)	SEM-AVS Ratio

Each sediment sampling event included at least one field blank (*i.e.,* for chemical analyses) and one field duplicate (*i.e.,* chemical analysis and toxicity testing). White quartz sand (Sigma Lot 67H0567), pre-cleaned with dilute HCl and thoroughly rinsed with de-ionized water, was used as the field blank sample for sediment analyses. Field duplicates were collected as described above, with approximately twice as much sediment collected and composited for the selected site, and then split into two duplicate samples, each transferred to appropriately cleaned and labeled sample containers. All sediment samples were stored on ice following collection. Upon completion of a sampling event, samples were transported under chain-of custody to PER, where they were placed in cold storage prior to shipment. Prior to shipment, a portion of each sediment sample was centrifuged and the porewater transferred to a separate container for pesticide concentration analysis. Where All samples were shipped to the analytical/testing laboratories within the holding time limits specified in the QAP. Sediment samples collected for chemical analysis were submitted to the CDFG-WPCL for chemical analysis. The chemical methods that were used for analysis of pesticides in sediment samples are shown in **Table 4**.

Water Sampling and Analysis

Water samples were collected prior to application, during application, and after application of aquatic pesticide to a water body. Conventional water quality parameter measurements (*e.g.,* pH, dissolved oxygen, temperature, and conductivity) were recorded for all sampling stations where water samples were collected (**Table 15**). The sampling procedure followed the methods described in the APMP Quality Assurance Plan (QAP). Briefly, all water samples were collected using "clean" techniques. Water samples for chemical analyses and toxicity assessments were collected by PER staff supported by one to two SFEI staff. Ambient water samples were collected into appropriately cleaned glass or HDPE containers using a peristaltic pump and pre-cleaned polyethylene and Tygon® tubing. Sample containers were triple-rinsed with site water prior to sample collection. Fresh sets of pre-cleaned tubing were used for each site.

Table 15. Conventional Water Quality Parameters

Parameters	**units**
Conductivity	µmho
Dissolved Organic Carbon	µg/L
Dissolved Oxygen (DO)	mg/L
Hardness (when salinity is < 5 $^{0}/_{00}$)	mg/L ($CaCO_3$)
PH	pH
Temperature	°C
Total Suspended Solids	mg/L
Alkalinity	mg/L (CaCO3)
Dissolved Calcium	mg/L
Dissolved Magnesium	mg/L
Dissolved Sodium	mg/L

During each event, an analytical chemistry field blank sample was prepared by pumping reverse osmosis, de-ionized water from the initial sample container into a separate pre-cleaned sample container. Field duplicate samples were collected as "side-by-side" samples using a 'Y' splitter attached to the tubing so two sample containers could simultaneously be filled. All ambient water samples for chemical analyses and toxicity testing were stored on ice immediately following collection. Upon completion of a days' sampling event, samples were either delivered directly to the testing laboratory or immediately transported to PER, where they were placed in cold storage. All samples were shipped to the analytical/testing laboratory within the holding time limits specified in the QAP. Water samples collected for chemical analysis were submitted to the CDFG-WPCL.

The chemical methods that were used for analysis of pesticides in water samples are shown in **Table 4**. The SOPs for these methods are shown in **Appendix 1**.

Tissue Sampling

Rainbow trout, Sacramento suckers (*Catostomus occidentalis*), and crayfish (*Pacifastacus leniusculus*) were collected from the MID Main Canal. These tissue samples were analyzed by CDFG-WPCL. The fish and crayfish were collected using a beach seine. Three to five specimens of identical species were wrapped in Teflon sheets, placed in a large polyethylene bags and stored on dry ice. Upon completion of a days' sampling event, sampling were either delivered or shipped to CDFG-WPCL. The rainbow trout were filleted and only muscle tissue analyzed. The California suckers were analyzed for whole body pesticide content. Crayfish were homogenized and analyzed for whole body pesticide content.

Toxicity Testing

The toxicity component of the APMP consisted of water and sediment samples taken from specific sites for conducting acute and chronic toxicity tests. Water and sediment samples taken for testing at a given sampling site were collected from the same water mass as the water chemistry samples, handled, and utilized as detailed in the QAP. All toxicity testing was complemented by a full chemical analysis of test water and sediments.

To conform with U.S. Environmental Protection Agency (1991) recommendations regarding ambient sample toxicity testing, and to provide consistency with existing SWRCB monitoring and assessment programs (e.g., SWAMP), workgroup members recommended using the U.S. EPA approach of testing water samples with the three standard EPA species (*Selenastrum capricornutum, Ceriodaphnia dubia, Pimephales promelas*). Where appropriate, larval rainbow trout were also used. For particle-bound pesticides that may pose risk to benthic species, the workgroup used sediment toxicity test protocols recommended by U.S. EPA for *Hyalella azteca* (EPA 2000). Sediment toxicity testing was conducted by either the University of California, Davis–Marine Pollution Studies Lab (UCD–MPSL) or PER. Water toxicity testing was conducted by

either the CDFG–Aquatic Toxicology Laboratory or the UCD–Aquatic Toxicology Laboratory.

Quality Assurance and Control

The APMP QAP addresses the details of the field and laboratory QA/QC procedures. The data quality criteria (DQCs) and performance standards defined in the QAP insure the levels of confidence and certainty in the environmental data. Individual contract laboratories selected to work for APMP are required to meet performance-based protocols that include initial and ongoing demonstration of laboratory capability. More detailed information of the QA/QC procedures for the APMP can be found in the QAP, which is included as **Appendix 2**. In addition, the quality control plans and SOPs from the chemical and aquatic toxicity contract laboratories are available from SFEI. The target method detection limits of the aquatic pesticides for water and sediment samples are shown in **Table 16**.

Table 16. Target Method Detection Limits for Pesticides

Medium	Compound	Target MDL
Water	Acrolein	0.2 µg/L
	Copper	1.0 µg/L
	2,4-D	0.005 µg/L
	Diquat dibromide	0.72 µg/L
	Fluridone	0.5 µg/L SePRO ELISA method
		0.001 µg/L HPLC-MS
		0.05 µg/L HPLC-Fluorescence
	Glyphosate	5.00 µg/L
	Endothal	TBD
	Methoprene	TBD
Sediment	Copper	1.0 mg/kg w/ Electrothermal AAS
		40 mg/kg w/ Flame AAS
	2,4-D	0.1 µg/kg
	Fluridone	2.00 µg/kg HPLC-MS
		25.00 µg/kg HPLC- Fluorescence
	Methoprene	TBD
Tissue		
	Copper	1.0 µg/kg
	2,4-D	0.1 µg/kg
	Fluridone	2.00 µg/kg
	Methoprene	TBD

Data Management

The contract laboratories provided analytical data and associated quality control information to the APMP by electronic transmission in various spreadsheet formats and as hard copies. Only data that have met data quality criteria or data that have explained

deviations appropriately were accepted from the laboratory. The data that were received electronically were then converted to standard APMP database format for final QA/QC checks. The data reports are included in the **Appendices 2-6**. As part of the APMP QAP, all data was validated per USEPA Data Validation Procedures.

RESULTS AND DISCUSSION

Acrolein

Acrolein was applied in the Livingston Canal August 13, 2002 by the Merced Irrigation District. This canal is a primary water delivery canal, approximately 4.5m wide and 2m deep, flowing at approximately 160 cubic feet per second. This canal is treated approximately every three weeks throughout the summer months to remove American Pond weed and algae. Water samples were collected before pesticide application, at 2 hours (h) post application, and at 72 h post application (**Figure 3**). The sample matrix is shown in **Table 9**. The acrolein data is shown in **Appendix 3**. Chemical analysis results showed that acrolein was present in water samples at 2 h post application (range 4500-4600 µg/L, mean concentration 4550 µg/L or ppb) and it was not detected at 72 h post application. Not finding acrolein in the 72 h post application sample was unexpected given that the Baker Test kit (a field colorimeter designed for acrolein detection) indicated the presence of acrolein and is far less sensitive than the CDFG-WPCL methods. The chemical analysis results confirm that a field chemical derivitization method or improved field sampling techniques need to be developed for stabilizing acrolein in collected water samples. Acrolein's high volatility and rapid breakdown contribute to the difficulty in obtaining accurate concentrations in samples collected in the field. Currently derivitization takes place in the laboratory within 24 h after the sample has been collected.

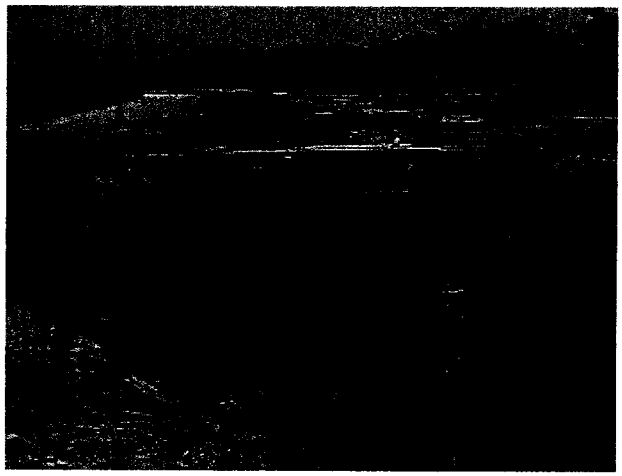

Figure 3. Livingston Canal t+72h sampling location

Toxicity testing was not conducted on environmental (water and sediment) samples collected from this site because it was predetermined from the literature review that acrolein both volatilizes and has a short degradation half life. By the time a water sample could be collected and a toxicity test set up and initiated, the acrolein concentrations would have degraded to a point where clear experimental results could not have been achieved.

Future plans for Phase 2 (2003) of the Project will include adding more field sampling sites for monitoring acrolein, developing a field chemical derivitization method or improved sampling techniques and, possibly, conducting in situ invertebrate and/or fish toxicity testing at sampling sites.

Copper

Copper concentrations and toxicity were monitored in four Marin Municipal Water District (MMWD) reservoirs during Phase 1 (2002). Two reservoirs received copper treatments (Nicasio and Bon Tempe Reservoirs) and two were selected as reference sites (Soulajule Reservoir and Lake Lagunitas). Nicasio and Soulajule reservoirs are located in the West Marin watershed (**Figure 4**). Lake Lagunitas and Bon Tempe reservoir are located in the Mount Tamalpais watershed. These reservoirs are all fed solely by rainfall runoff. These are no human contact reservoirs but are stocked with fish. The sample matrix is shown in **Table 10a, and 10b**. The chemical and toxicity testing data are shown in **Appendix 4**.

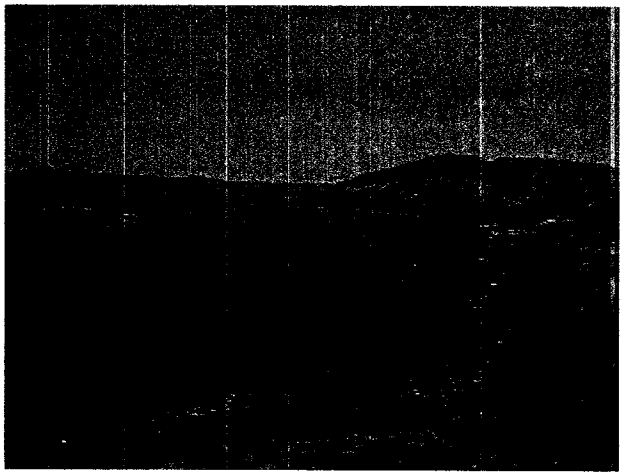

Figure 4. Nicasio Reservoir August 2002

Nicasio Reservoir was treated for floating algae with copper sulfate. Copper was applied by dissolution of granular copper sulfate in burlap bags towed behind a boat. Results of sediment toxicity tests at Nicasio Reservoir were compared to sediment tests conducted at Soulajule Reservoir, a waterbody that has never been treated. The initial plan was to collect water and sediment for chemical analysis and toxicity testing in Nicasio Reservoir. However, due to timing issues (MMWD stopped drawing water from Nicasio Reservoir and suspended treatment) only a preapplication water sample was collected. Sediment samples were collected from both Nicasio and Soulajule Reservoirs. Copper was measured in a single water sample. Copper was measured in all bulk-phase sediment and porewater samples tested for toxicity. Chemical analyses for copper in the two West Marin Watershed reservoirs is summarized in **Table 17**.

Table 17. Copper Concentrations in West Marin Watershed Reservoirs

	Water		Porewater		Sediment	
	Dissolved (µg/L)	Total (µg/L)	Dissolved (µg/L)	Total (µg/L)	Dry Weight (mg/kg)	Wet Weight (mg/kg)
Soulajule Reservoir (reference site)	2	3.9	<1.0-2.6	<1.0-45.7	40.2-49	16.3-17.9
Nicasio Reservoir	NA	NA	<1.0-22.7	<1.0-23.5	32.6-104	23.2-51.1

Bon Tempe Reservoir was treated with granulated copper sulfate for benthic algae control. Granulated copper was applied with a hopper mounted to an airboat. Lake Lagunitas, was selected as a reference site for comparison purposes, and was not treated with copper. Bulk-phase and porewater copper concentrations were measured in samples

from these two reservoirs. Samples were also tested for toxicity. Chemical analyses for copper in the two Mount Tamalpais watershed reservoirs is summarized in **Table 18**.

Table 18. Copper Concentrations in Mount Tamalpais Watershed Reservoirs

	Porewater		Sediment	
	Dissolved (µg/L)	Total (µg/L)	Dry Weight (mg/kg)	Wet Weight mg/kg
Lake Lagunitas (reference site)	<1.0	8.2-10.8	18-34.4	7.4-8.1
Bon Tempe Reservoir	6.7-352	64.4-11,900	250-1,113	143-770

The concentrations of copper found in sediment samples from Nicasio and Bon Tempe Reservoirs were higher than the two reference reservoirs (Soulajule Reservoir and Lake Lagunitas). However, this was not the case for porewater samples where the maximum total copper concentration in Nicasio Reservoir (23.5 µg/L) was generally less than the maximum level found in Soulajule Reservoir (45.7 µg/L), Nicasio's reference site reservoir. Bon Tempe Reservoir had the highest level of total copper in porewater (Sample B 05 total 11,900 µg/L).

Toxicity of these samples was assessed using two protocols. Toxicity of all samples was assessed with the 10-d growth and survival test with the amphipod *Hyalella azteca*. Toxicity of a subset of samples was also measured with the 28-d growth and survival test with this species. No sediment samples from Nicasio, Soulajule, or Lake Lagunitas Reservoirs were toxic to *Hyalella azteca* in either the 10-d or 28-d exposures. Mean survival was greater than 83% in all of these samples. Significant reduction in amphipod survival occurred in sediment sampled from Bon Tempe station B-01 (33% survival). This station had the highest dissolved copper concentration in porewater (352 µg/L). The 10-d LC50 for copper toxicity to *Hyalella azteca* is 35 µg/L (Phipps et al. 1995). No amphipods survived in the B-01 sample after 28-d. Amphipod survival in the remaining Bon Tempe Reservoir samples was not significantly lower than in the control samples.

During Phase 2 (2003) of the project, additional drinking water reservoirs throughout the state will be monitored for copper. Benthic community bioassessments are also planned for locations that receive large amounts of copper sulfate.

Fluridone

Fluridone was monitored in Clear Lake (Lake County) where it was applied in pellet form for control of the aquatic weed *Hydrilla verticillata*. It is applied to the near shore area with a hopper mounted on an airboat. The shore of Clear Lake is divided into 80 sections (**Figure 5**). Each section is monitored for the presence of Hydrilla and treated according to the degree of infestation. Clear Lake is used primarily for recreation. The lake has a large surface area, but generally shallow. Sediment samples were collected from seven sites (treated and untreated) around the lake. The sample matrix is shown in **Table 11**. The Clear Lake fluridone chemical and toxicity testing results are shown in the **Appendix 5**.

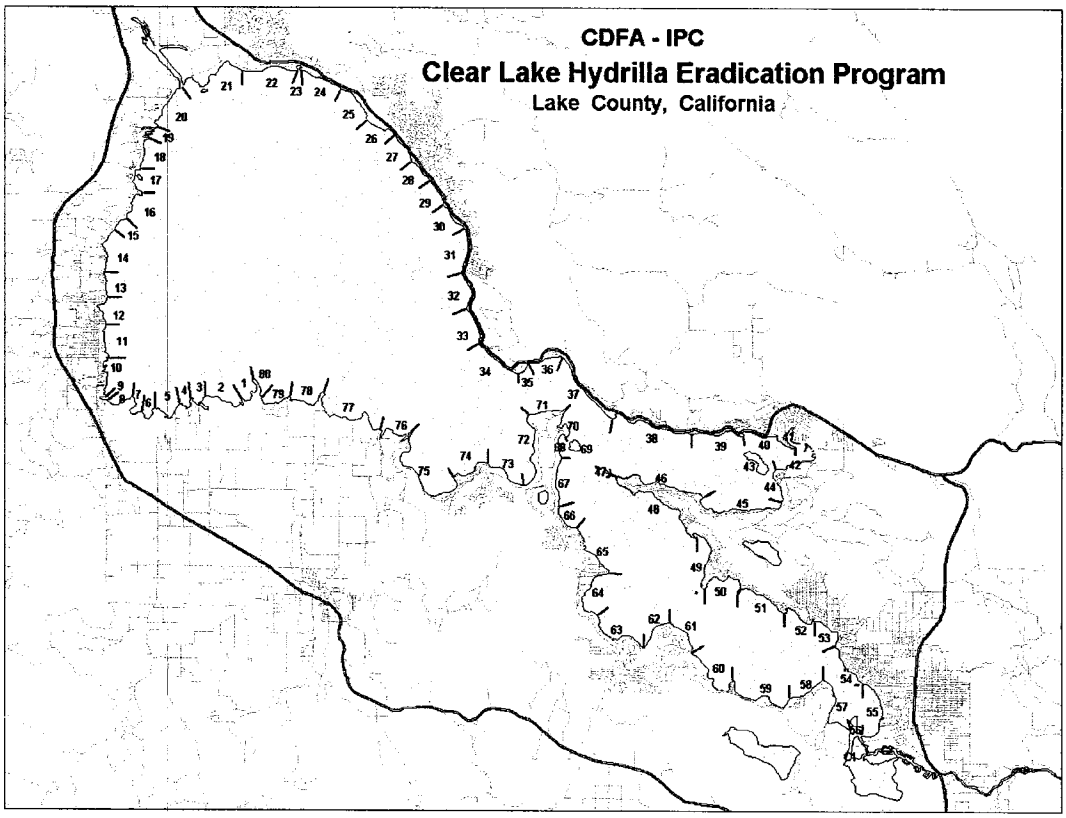

Figure 5. Fluridone treatment zones in near shore areas of Clear Lake, California.

Fluridone was found in both treated and untreated sediment samples (**Table 19**). It was found in porewater samples from treated sediment but was not detected in porewater samples from untreated sediment.

Table 19. Fluridone Concentration in Clear Lake Sediments

	Porewater (µg/L)	Total (µg/L)
Treated Sites	15.5-31.2	59.3-1625
Untreated Sites	ND	ND-98.8

ND=nondetect

Sediment toxicity testing included using acute 10-day and chronic 28-day survival and growth tests on the amphipod *Hyallela azteca* (Table 15). Acute 10-day toxicity tests showed a significant reduction in *Hyalella* growth in one untreated sediment sample versus the control sample. There was no indication of acute toxicity in any other sediment samples. Results of the 28-day survival and growth tests for two selected sediment samples showed a statistically significant reduction in *Hyalella* growth in the CLU01-STOX sediment, which was consistent with the reduction in growth observed in the acute test of this sediment sample, versus the control sample (mean % survival 96.25, mean dry wt 0.79 mg). It is hypothesized that the reduction in growth in the untreated CLU01-STOX sediment sample might be due to a growth inhibitor bound to the organic carbon of the sample (93,000 mg/kg). It is well documented that Clear Lake is contaminated with mercury in a variety of forms (including methyl mercury) and this mercury may be the cause of the sediment toxicity. There was also a statistically significant reduction in *Hyalella* survival in the CLT06-STOX sediment sample.

Table 20. Clear Lake Sediment Toxicity Test Results

Sample ID	Treated or Untreated Sample	Test Type (using *Hyallela azteca*)	Mean % Survival	Mean Dry Weight
Control		10-day	93.75	0.21
CLU01-STOX	Untreated	10-day	95.7	0.17
Control		28-day	96.25	.079
CLU01-STOX	Untreated	28-day	91.25	0.57
CLT06-STOX	Treated	28-day	82.5	0.81

During Phase 1 (2002), fluridone was also monitored in the Merced Irrigation District (MID) Main Canal. The MID Main Canal is the primary canal used for transferring water from the Merced River to growers within the district. The canal is approximately 30 miles long, 45 feet wide, and 12 feet deep during the growing season (**Figure 6**). During the growing season the canal terminates in Lake Yosemite. During the low flow season (November-March) the canal is 35 feet wide , on average 3 feet deep, and 20 miles long (not quite reaching Lake Yosemite). MID uses a liquid formulation

that is injected into the canal over a two-month period. Water, sediment, and tissue samples were collected and tested from this location. This sample plan is show in **Table 12**. The MID fluridone chemical and toxicity testing results are shown in **Appendix 6**.

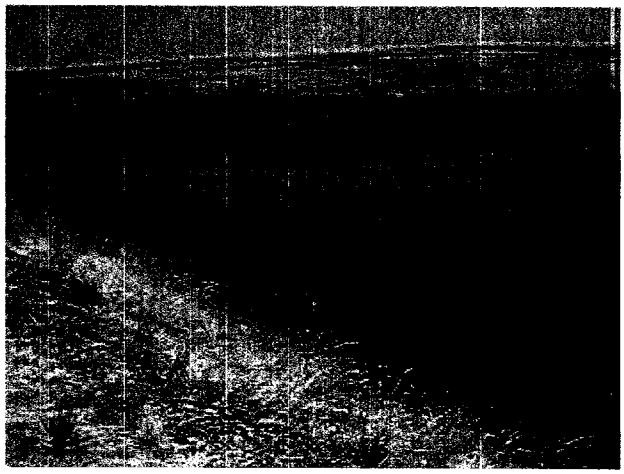

Figure 6. Typical view along MID Main Canal during irrigation season.

Pretreatment sampling indicated the presence of fluridone in some sediment samples and in the rainbow trout samples. The concentrations detected were in the low parts per trillion range. Fluridone tissue concentrations increased in all three species sampled two weeks after the cessation of treatment. However, at five weeks post treatment cessation all tissue concentraions were below detectable limits. The detection of fluridone in the pretreatment samples is of note because the most recent prior treatment with fluridone was in the fall of 2000. However, it was estimated by Applied Marine Sciences staff (whoa ssisted in the collection) that the age of the fish from the first two sampling events were approximately a year old. It is unlikely that they would be younger than that, however, they could also be much older (since size is highly dependent on food supply). CDF&G typically releases trout that are 1 year old and about that size. At the third sampling, a single much larger fish was caught and anaylzed. It was estimated that this fish was likely between three and five years old, but could have been as old as seven or eight.

Sediment and tissue samples collected after treatment cessation indicated accumulation in all matrices (**Tables 20 and 21**). A third tissue sample collection will take place on February 19, 2003.

Table 20. Tissue Concentrations from MID Main Canal

Sample Type	Treatment Phase	Fluridone Concentration (µg/L)
Rainbow Trout	Pretreatment	0.080-0.125
	2 Weeks Post Application	0.80
	5 Weeks Post Application	ND
Sacramento Suckers	Pretreatment	Not collected
	2 Weeks Post Application	0.72-1.21
	5 Weeks Post Application	ND
Crayfish	Pretreatment	ND
	2 Weeks Post Application	4.14-6.06
	5 Weeks Post Application	ND

ND=non detect

Table 21. Sediment Concentrations from MID Main Canal

Treatment Phase	Concentration (µg/L)
Pretreatment	ND-13.4
2 Weeks Post Application	7.56-76.8

ND=non detect

Glyphosate

Glyphosate was monitored in Orange County's Bolsa Chica Canal (near Garden Grove and Westminster, CA). This is a storm water drainage canal that is fed in the dry season by lawn sprinkler runoff. The canal emerges from underground culverts and flows approximately four miles through canal channel lined with rip rap, concrete culvert, or natural banks before terminating at Huntington Harbor. Throughout the dry season the water is not more than 8 inches deep throughout most of the canal. At the time of monitoring it was calculated that the flow rate was 0.44 mph. Only water samples were collected at this site because glyphosate is not bioavailable when it is bound to sediment. This sample matrix is shown in **Table 13**. The primary sampling location is shown in **Figure 7**. The chemical and toxicity testing data are shown in **Appendix 7**.

Figure 7. T=0, 2.5 h, 4.5 h, and 23 h sampling location in Bolsa Chica Canal

Glyphosate was measured in the water samples (range not detectable-820 µg/L, maximum concentration at 2.5 h post application). Toxicity was detected in several of the samples collected in the canal. One fathead minnow test (2.5 h post application) showed toxicity. However, it could not be determined if the observed toxicity was due to glyphosate or another toxicant. Total mortality of *Ceriodaphnia* was observed in two samples collected at 4.5 h and 24 h post application. An Enzyme-Linked Immunosorbent Assay (ELISA) tests were conducted for chlorpyrifos and diazinon. Both pesticides were found to be present at 1 Toxic Unit each. However, since the samples had been stored in plastic containers for nine days prior to analysis and it is known that organophosphate insecticides adsorb to plastic, it is highly likely that the concentrations of the two pesticides were higher at the time of sampling and toxicity testing.

During Phase 2 (2003), additional sites where system inputs can be better characterized will be identified and incorporated into the sampling program. In addition, samples collected from environments with multiple uncontrolled inputs will be analyzed for a wider range of compounds.

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 1.

1. *Which aquatic pesticides used in California have the highest "risk" of impacts to people and the environment?* This question has been reasonably well answered during Phase 1. Phase 2 will further refine our understanding of the potential pesticide "risk".
2. *What are the concentrations of the target aquatic pesticides in the environment (water, sediment, and biota) adjacent to their application point?* This question has begun to be addressed for the four initial pesticides monitored for. Additional application points and pesticides will be added for Phase 2 and tissue sampling will be expanded.
3. *Are the measured concentrations above existing effects thresholds?* This question has not yet been answered.
4. *Which locations have the highest "risk" of beneficial use impairment?* Addressed somewhat in Phase 1 plan, but will be more thoroughly evaluated in Phase 2.
5. *What is the degree of biological impacts to non-target biota from application and exposure to aquatic pesticides?* Toxicity testing addressed this question to some degree. During Phase 2 bioassessments will be developed and conducted that will address this question directly.
6. *What Best Management Practices are currently being used to mitigate potential impacts from aquatic pesticide application?* BMPs have not been investigated and there is not yet enough data to evaluate label instructions.

Phase 2 (2003) Proposed Sampling Plan

In its second year, the APMP will undertake a larger-scale monitoring program to be implemented during Phase 2 (2003). The Tier 1 and 2 studies will be conducted during Phase 1 will be continued. Initially, Phase 1 sampling was conducted in 2002 as a

preliminary study of pesticide fate under worse case scenarios. Measurements included chemistry and toxicity testing of water and sediment samples. Phase 2 monitoring in 2003 will build upon the first years' experience and will use a triad sampling approach as recommended by the EPA, that will entail the simultaneous collection of chemistry, toxicity, and bioassessment data. Bioassessments will focus on communities that are widely recognized in the scientific literature as good biological indicators of perturbation: aquatic invertebrates, macrophytes, and phytoplankton. Due to the diverse nature of the target pesticides and water body types studied, the type of bioassessments conducted will be specifically tailored for each pesticide sampling events. This workplan summarizes the objectives, technical approach, sampling methods, and schedules to be performed of the Phase 2 sampling program. This work plan summarizes the project goals, study design, and sampling protocols and schedules to be performed during Phase 2 of the APMP. This should be considered a draft plan and it is currently undergoing further technical review.

Objectives

The APMP proposes to conduct biological monitoring studies, in concert with chemical and toxicological testing, in order to assess the short-term and cumulative impact of pesticide use on non-target plants and animals. The specific objectives of the research are as follows:

1) Evaluate the effects of pesticides on non-target aquatic biological communities:
    a. *Determine the effect of chronic pesticide exposure on benthic macroinvertebrates.* Community structure elements to be assessed include taxonomic, functional, and tolerance composition, along with abundance and diversity measures.
    b. *Determine the effects of pesticide applications on the macrophyte community and associated epiphytic macroinvertebrates.* Effects could include pesticide drift and changes in water column chemistry from pesticide decomposition of aquatic vegetation. Community structure elements to be assessed for macrophytes include taxonomic composition, frequency distribution, coverage, abundance, and diversity measures. Epiphytic macroinvertebrates will be analyzed for the same community structure elements as the benthic invertebrates.
    c. *Determine the effect of chronic pesticide exposure on phytoplankton communities.* Community structure elements to be assessed include taxonomic composition, abundance, and diversity measures.

2) Evaluate the acute lethal effects of pesticides on resident aquatic organisms through toxicity testing.

3) Evaluate the sublethal effects of pesticides on resident aquatic organisms. This entails assessment of potential biochemical and/or physiological effects by toxicity testing.

4) Evaluate the potential for pesticides to bioaccumulate in resident organisms. The chemistry of tissue samples will be assessed.

5) Conduct experiments and collect data for calibration and validation of the EXAMSII fate and assessment model.

Approach

Sampling Strategy

The goal of Phase 2 monitoring is to sample commonly used aquatic pesticides from a diverse range of water body types that are located at various regions throughout California. The frequency and level of sampling varying depending on the pesticide and will depend upon site-specific issues (e.g. presence of other potential contaminants, availability of reference sites). The pesticides to be monitored during Phase 2 include 2,4-D, copper sulfate, chelated copper, diquat dibromide, endothall, fluridone, glyphosate, malathion, methoprene, and triclopyr. Due to the extremly volatile nature of acrolein, as seen from Phase 1 results, sampling for Acrolein will focus on developing an accurate field sampling method with appropriate detection sensitivity. Therefore, only water samples will be collected for the presence/absence of acrolein.

Sampling activities will be organized into five tasks.

- Task 1. Conduct a pilot study using intensive, repeated-measures sampling of three to four pesticides, at three to four site locations that have had chronic pesticide application over the past several years utilizing the triad approach. The sampling will be conducted early season (spring) and will provide a preliminary evaluation of potential effects to biological communities. This pilot study can then guide later season sampling efforts.

- Task 2. Conduct short-term survey sampling of pesticides utilizing the triad approach. Data from the Phase 2 pilot study will be evaluated and then

incorporated, and an appropriate scope of analysis will be determined for bioassessment sampling. If pilot study data is not available in time to conduct the rest of the season sampling, bioassessments will be conducted as cost and time allows.

- Task 3. Conduct intensive toxicity special studies where appropriate. These studies include non-ionic surfactant analysis using endocrine system disruption type assays and toxicity identification evaluations (TIEs), laboratory plant bioassays, tissue bioaccumulation analysis, and in-situ toxicity testing and life cycle bioassessments.
- Task 4. Data analysis.
- Task 5. Draft and final report writing.

Sampling Program Design

To meet the objectives and provide consistency with Phase 1 sampling, a temporally stratified study design will be implemented to coincide with pesticide application events. A worst-case scenario design will yield data on both acute and chronic pesticide impacts. The proposed sampling frequency will enable detection of potential biological responses as macroinvertebrates, and to a lesser extent, phytoplankton and macrophytes can respond within weeks to a perturbation. Samples will be collected before pesticide application and at various post application increments (**Table 22**). We will conduct quantitative sampling to enable spatial and temporal statistical comparisons.

Table 22. Sampling frequency, collection order, and proposed locations.

Sample collection frequency
Pre-application
Initial Post-application (within 1-24 hrs)[1]
2 weeks post
4-6 weeks post**
Post-application season (after 3-4 months)[2]
Order of Sample Collection
1. Physical Habitat Assessment
2. Water Quality Parameters
3. Macrophyte Survey
4. Sediment Parameters
5. Macroinvertebrate Assessments
Proposed Sampling Sites[3]
Site / Control Site / Pesticide
Lake Bon Tempe / Lake Lagunitas / Copper Sulfate[4]
Costa Ponds / untreated Costa Ponds / Fluridone[4]
Lower Stone Lake / Northern Stone Lake / Glyphosate[4]
Clear Lake / untreated area within lake / Fluridone
Stone Lake treated canal / Stone Lake un-treated canal / 2,4-D
Nicasio Reservoir / Soulajule Reservoir / Copper Sulfate
Solano ID treated canal / ? / Chelated Copper
Potter Valley ID treated canal / ? / Chelated Copper
Big Bear Lake / ? / Fluridone
Contra Costa VCD pond / untreated area / Methoprene
SF Bay site / ? / Glyphosate

[1] Macrophytes not collected at this time.
[2] For pilot study sampling only.
[3] Proposed sampling sites identified as of March 20, 2003. Sites subject to change after initial site visits.
[4] Pilot Study sites.

Sample Collection Methods

Sampling for bioassessments will be 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 (Harrison and Born 1999), and these will be adapted and used. Control sites for each location will be identified, and sampled using the same methodology as treated sites. Pre-application sampling may substitute for reference sampling if no suitable control site is found. Global Positioning System (GPS) coordinates will be recorded for each sampling station.

Benthic Macroinvertebrates

Benthic samples will be collected with a Petite Ponar sampler in the immediate vicinity of pesticide application (pre-sampling will also take place in this general area). For lentic systems, a minimum of two sampling stations within the total application zone

will be located and sampled. Three replicate samples will be randomly collected from a 10 x 10 meter area within each sampling station. A minimum of six total samples will be collected at each site location, with a total of twelve (includes control site) per sampling event. Collection of ancillary water and sediment measurements, toxicity testing, and organism tissue collection will occur within close proximity to benthic collection and in the appropriate collection order (**Table 23**).

For lotic systems, sampling stations will be selected in a linear manner in reference to the application point. One control reach will be located 5-10 meters upstream of the application point. Two sample reaches of equal length (minimum of 5 meters) will be established sequentially downstream of the application point. For soft bottom systems, samples will be collected using a Petite Ponar. Three replicate samples will be randomly collected from within each sampling reach and from within the control reach, for a total of nine samples collected at each sampling event. For cobble/rock/large woody debris bottoms, samples will be collected using kick nets as outlined in the California Stream Bioassessment Procedure (CDFG 1999). Three transects will be randomly selected within each reach, with potential transect points located at one meter intervals along the bank. BMIs will be collected with kick nets from three locations along each transect. The three samples will be combined into a single composite sample. The control reach will be sampled using the same design. The total number of samples collected per sampling event will be nine.

The material from each benthic grab will be sieved using a 0.5 mm sieve bucket, and the retained material transferred into a labeled 500 mL plastic wide mouth jar and preserved with 95% ethanol and organism stain. The preserved samples will be transported, under chain of custody, to the laboratory where they will be processed following standard procedures. Organisms will be identified at the Level 2 taxonomic effort in accordance with the CAMLnet Standard Taxonomic Effort List (CDFG 2003) (**Table 23**).

Table 23. Macroinvertebrate, Macrophyte, and Phytoplankton Biometrics

Metric	Unit
Benthic Macroinvertebrates	
Abundance	Total Number
Richness	Total Number of Individual Taxa
Diversity	Shannon-Weaver Index
EPT Taxa	%
Intolerant Organisms	%
Tolerant Organisms	%
Dominant Taxa	%
Collector	%
Filterer	%
Scraper	%
Predators	%
Shredders	%
Diptera Richness	%
Chironomidae Richness	%
Oligochaeata Richness	%
Epiphytic Macroinvertebrates	
Abundance/ Sweep	Total Number
Richness	Total Number of Individual Taxa
Diversity	Shannon-Weaver Index
EPT Taxa	%
Intolerant Organisms	%
Tolerant Organisms	%
Dominant Taxa	%
Functional Feeding Group	%
Diptera Richness	%
Oligochaeata Richness	%
Macrophytes	
Abundance	Total # of occurrences
Frequency of Occurrence	# intercepts/total intercepts for each species
Coverage	Interval area / total transect area for each species (areas estimated)
Species Diversity	Average number of species per interval
Dominant Taxa	% Present
Invasive Taxa	% Present
Occurrence by Structural Morphology	%
Phytoplankton	
Abundance	Total Number
Diversity	Total Number of Individual Taxa
Richness	Shannon-Weaver Index

Epiphytic Macroinvertebrates

For lentic systems, epiphytic macroinvertebrates will be sampled utilizing a transect design as outlined in the California Lentic Bioassessment Procedure (CDFG 2002). However, only two transects will be established running perpendicular to the pesticide application zone. Length will be variable, and transects will run from near the

shorel out to center of the application zone. For the sake of time, transects will be marked by GPS coordinates only and not physically set. Water depth will be recorded at the beginning and end of each transect and at each sample interval. Transects should be chosen for habitat homogeneity and representation of the average conditions within the area of interest. Three qualitative sweeps of standard effort (1-3 minutes) should be taken within the submerged/emergent pelagic vegetation and within the littoral vegetation up to the shoreline along each transect. The sweeps should be combined to produce one composite sample within a plastic wide mouth jar containing preservative. The number of samples for each site will be two, with a total of four for each sampling event.

Within lotic systems, sampling stations will be established in a linear manner in reference to the application point. The control site will be located 5-10 meters upstream of the application point. Two sample reaches of equal length (minimum of 5 meters) will be located sequentially downstream of the application point. Three qualitative sweeps of standard effort (1-3 minutes) should be taken within the littoral vegetation of each reach. The sweeps should be combined to produce one composite sample within a plastic wide mouth jar containing preservative. One composite sample will be collected from the control reach. The total number of composite samples for each sampling event will be 3.

The preserved samples will be transported, under chain of custody, to the laboratory where they will be processed following standard procedures. Organisms will be identified at the Level 2 taxonomic effort in accordance with the CAMLnet Standard Taxonomic Effort List (CDFG 2003) (**Table 23**).

Macrophytes

Macrophytes will be quantitatively sampled using a line intercept method as adapted from Madsen (1999). Presence/absence techniques will be employed to rapidly gather large amounts of data on which statistical analysis (Chi-square, t-tests) can be performed to determine potential herbicide affects to non-target macrophytes (**Table 23**).

For lentic systems, transects will be established on the site by GPS coordinates within the treated and non-treated areas. Water depth will be recorded at the beginning and end of each transect and at each sample interval. Sediment type will also be recorded at each interval. The two treated transects that are set up for macroinvertebrate work will

also be used for macrophytes. Macrophyte data will be collected prior to BMIs to reduce disturbance during the visual survey (**Table 22**). Two control transects (equal in length to the treated transects) will be established in an untreated area. Habitat for all four transects should be as analogous as possible. Sample intervals will be every meter along the transects. From a boat or wading, species presence and absence will be noted at each sampling interval and recorded on a datasheet. Species are present when they intersect the plane of the line segment (1 m in length) from the bottom to the surface. In low visibility waters, submerged plants can be observed with a viewing tube. Underestimates of submerged vegetation may occur due to visibility issues. Rakes and scuba diving could be employed but these methods are time-consuming and the level of effort expended for the data collected should be considered (e.g. it will be difficult to representatively sample non-target submersed species with only a few rake throws). Species with questionable identifications will be collected in plastic bags and given to a qualified taxonomist for more thorough identification.

For lotic systems, the transects set up for the macroinvertbrate sampling will be used to collect macrophyte data. However, only two transects within each reach will be surveyed, and the randomly chosen transect locations marked by GPS coordinates. Sample intervals will be every meter along the transects. Macrophyte data will be collected prior to BMIs (**Table 22**). Record presence/absence data as stated above.

Phytoplankton

Phytoplankton assemblages have high seasonal variability and collection during one field sampling season will yield snapshot information only on the potential impacts from herbicide use. Sample analysis of algae can be costly as well. Therefore, phytoplankton will only be sampled at two of the intensively studied sites this season.

Within the application zone only, phytoplankton will be collected using a peristaltic pump to pass a known quantity of water (1 m below surface) over a filtering sieve (USGS 1989). Samples will be collected from where water quality samples are taken. Two samples per site should be collected. Samples will be placed in a 100 mL polyethylene bottle preserved with 1 mL of Lugol's solution. The preserved samples will be transported, under chain of custody, to the laboratory where they will be processed

following standard procedures. Samples will be counted and identified in the laboratory following standard procedures (**Table 23**).

Special Toxicity Studies

Studies to be conducted include surfactant analysis using endocrine system disruption type assays, development of toxicity identification evaluations (TIEs) for individual pesticides where needed, laboratory plant bioassays, bioaccumulation analysis, and in-situ toxicity testing and life cycle bioassessments (**Table 24**). Most of the studies will be conducted in the laboratory, with the exception of some in-situ testing and bioaccumulation tissue collection. Qualified labs will conduct the studies following standardized procedures. These tests will be conducted as follows:

Table 24. Special Toxicity Studies

Study	Target Pesticide	Test Species	Endpoint
Plant Bioassay	Fluridone, 2,4-D	*Typha spp.*	Seed germination
Surfactant/TIE	Diquat, Endothall, Glyphosate	Fish, ESA fish species	% Survival, Endocrine disruption
In-situ sediment toxicity testing	Methoprene	*Chironomous tetanus* or *riparius; Hyallela az.*	Morphological deformities, life-cycle disruptions, mortality
Bioaccumulation	Copper Sulfate, Fluridone, 2,4-D	Bivalves	Comparison to literature threshold concentrations

Model Validation Experiments

The EXAMSII Model is suitable for use in aquatic systems with well-defined inputs and hydrodynamics. Detailed site information needs to be collected in order to feed into the EXAMSII fate and assessment model, and these measures have been incorporated into the conventional parameters to be collected at every site (**see Table 25**). Field experiments using conservative tracer/dye will be conducted at 1-2 site location to be determined following site inspections. A conservative agent will be 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. This will allow accurate parameter input into the model.

Habitat Assessment

A determination of habitat quality will be made at each sampling site during every collection by measuring various physiochemical parameters (**Table 25**).

Table 25. Conventional Parameters Measured

Physical Parameters	**Units**
Air Temperature	°C
Water depth	M
Sediment collection depth	Cm
Geometric profiles of water body	Cross-sections/ diagrams
Flow Rate (lotic systems)	Cfs (ft3/s)
Inflow Volume (lotic systems)	Cc
Outflow Volume (lotic systems)	Cc
Flow Diversions	Describe
Current from wind action (lentic systems)	Qualitative – none, mild, moderate, strong
Anthropogenic activities/ alterations	Describe
Wildlife presence	Describe
Conventional Water Quality Parameters	**Units**
Conductivity	µmho
Dissolved Organic Carbon	µg/L
Dissolved Oxygen (DO)	mg/L
Hardness (when salinity is < 5 $^{0}/_{00}$)	mg/L ($CaCO_3$)
Salinity	psu (‰)
PH	PH
Temperature	°C
Total Chlorophyll a	mg/m^3
Total Phosphorous	mg/L – P
Total Nitrogen	mg/L – N
Total Suspended Solids	mg/L
Alkalinity	mg/L ($CaCO_3$)
Dissolved Calcium	mg/L
Dissolved Magnesium	mg/L
Dissolved Sodium	mg/L
Turbidity	NTU
Sediment Quality Parameters	**Units**
% gravel (> 2 millimeters)	% dry weight
% sand (2 mm > 62 µm)	% dry weight
% fines (< 62 µm)	% dry weight
Nitrate-Nitrogen	mg/kg
% solids	% dry weight
% moisture	% dry weight
Temperature	°C
Total Nitrogen	mg/kg
Total Organic Carbon	mg/kg
Pore Water Pesticide Concentration	mg/l or µg/L
SEM-AVS (for copper treatments only)	SEM-AVS Ratio
Eh	MV

Note: When sampling lotic systems, the 'Physical Habitat Quality' datasheet from the California Stream Bioassessment Procedure (CDFG 1999) shall also be used.

References

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

CDFG. California Department of Fish and Game. 2002. California Lentic Bioassessment Procedure (Protocol Brief for Biological Sampling for Lakes and Reservoirs). Revision date July 2002. California Department of Fish and Game, Water Pollution Control Laboratory /Aquatic Bioassessment Laboratory, Rancho Cordova, CA.

CDFG. California Department of Fish and Game. 1999. California Stream Bioassessment Procedure (Protocol Brief for Biological and Physical/Habitat Assessment in Wadeable Streams) Revision date May 1999. California Department of Fish and Game, Water Pollution Control Laboratory /Aquatic Bioassessment Laboratory, Rancho Cordova, CA.

Madsen, J.D. 1999. Point Intercept and Line Intercept Methods for Aquatic Plant Management. Aquatic Plant Control Technical Notes Collection (TN APCRP- MI-02). U.S. Army Engineer Research and Development Center, Vicksburg, MS.

Ode, P. 2003. CAMLnet: List of Californian Macroinvertebrate Taxa and Standard Taxonomic Effort. Revision date January 27, 2003. California Department of Fish and Game, Water Pollution Control Laboratory /Aquatic Bioassessment Laboratory, Rancho Cordova, CA.

US EPA. United States Environmental Protection Agency. 2003. Biological Indicators of Watershed Health at: http://www.epa.gov/bioindicators/html/indicator.html

USGS. United States Geological Survey. 1989. Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. In: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A4, pp. 99-113.

Appendices

Appendix 1. APMP Chemical Method Statement of Procedures (SOPs)
Appendix 2. APMP 2002 Quality Assurance Project Plan
Appendix 3. Acrolein Data From Merced Irrigation District Livingston Canal
Appendix 4. Copper Data From Marin Municipal Water District Reservoirs
Appendix 5. Fluridone Data From Clear Lake
Appendix 6. Fluridone Data From Merced Irrigation District Main Canal
Appendix 7. Glyphosate Data From Orange County Bolsa Chica Canal