UNIVERSITY OF CALIFORNIA, DAVIS

BERKELEY • DAVIS • IRVINE • LOS ANGELES • MERCED • RIVERSIDE • SAN DIEGO • SAN FRANCISCO • SANTA BARBARA • SANTA CRUZ

JOHN MUIR INSTITUTE OF THE ENVIRONMENT

ONE SHIELDS AVENUE
DAVIS, CALIFORNIA 95616-8576

QUALITY ASSURANCE PROJECT PLAN

(QAPP)

FINAL

Sacramento and San Joaquin River Basins and Sacramento-San Joaquin Delta TMDL Monitoring for Organophosphorus Pesticides and Other Pesticides Identified as Posing a High Risk to Surface Waters

SWAMP Project ID 02TM5001

(Revision 0.0)

Prepared By

Henry Calanchini

26 January 2006

GROUP A: PROJECT MANAGEMENT

1. APPROVAL SIGNATURES

Aquatic Ecosystems Analysis Laboratory, John Muir Institute of the Environment, University of California, Davis

Title:	Name:	Signature:	Date:
Project Manager	Michael Johnson		
QA Officer	Melissa Turner		
Project Supervisor	Henry Calanchini		

California Department of Fish and Game's Water Pollution Control Laboratory, Rancho Cordova

Title:	Name:	Signature:	Date:
CDFG Quality Assurance Officer	Loc Nguyen		
CDFG Lab Contract Manager	Dave Crane		

Central Valley Regional Water Quality Control Board

Title:	Name:	Signature:	Date:
Contract Manager	Jay Rowan		
Project Manager	Petra Lee		
Quality Assurance Officer	Leticia Valadez		

2. TABLE OF CONTENTS

LIST OF APPENDICES

This Page Intentionally Blank

3. DISTRIBUTION LIST

Title:	Name (Affiliation):	Tel. No.:	QAPP No:
Contractor Project Manager	Michael Johnson	(530) 752-8837	
Contractor Project Supervisor	Henry Calanchini	(530) 297-4684	
Contractor QA Officer	Melissa Turner	(530) 297-4684	
Regional Board Contract Manager	Jay Rowan (CVRWQCB)	(916) 464-4718	
Regional Board Project Manager	Petra Lee (CVRWQCB)	(916) 464-4603	
Regional Board QA Officer	Leticia Valadez	(916) 464-4634	
Chief, Sacramento River TMDL Unit	Joe Karkoski (CVRWQCB)	(916) 464-4668	
CDFG Lab Contract Manager	Dave Crane	(916) 358-2859	
CDFG QA Officer	Loc Nguyen	(916) 358-0314	

4. PROJECT/TASK ORGANIZATION

4.1 Involved parties and roles.

The Central Valley Regional Water Quality Control Board (CVRWQCB) is a California state regional board tasked with protecting the quality of the waters within the Central Valley Region for all beneficial uses. The CVRWQCB formulates and adopts water quality control plans for specific ground and surface water basins and prescribes and enforces requirements on waste discharges. As the contracting agency, CVRWQCB will direct UC Davis staff in sample collection techniques, sampling site locations, sampling frequency and duration and the initiation and maintenance of a contract with the California Department of Fish and Game's (CDFG) Water Pollution Control Laboratory (WPCL).

The Aquatic Ecosystems Analysis Lab (AEAL) of the John Muir Institute of Ecology at UC Davis is responsible for the collection of water samples and their delivery to CDFG's Water Pollution Control Laboratory. AEAL will create and populate a database of project results and maintain copies of field sheets and chain of custody forms. AEAL will maintain contact with the Regional Board and CDFG to notify of intent to sample and provide the CVRWQCB with updates on sampling progress. At the completion of monitoring, AEAL will prepare a final report to the CVRWQCB (see Table 2 for timeline).

The CDFG Water Pollution Control Laboratory in Rancho Cordova will be the contract laboratory for all analyses. CDFG will analyze submitted samples in accordance with all method and quality assurance requirements found in this QAPP. CDFG will act as a technical resource to UC Davis staff and management.

Table 1. (Element 4) Personnel responsibilities.

Name	Organizational Affiliation	Title	Contact Information
Jay Rowan	CVRWQCB	Contract Manager	Ph: (916) 464-4718 Fax: (916) 464-4800 jrowan@waterboards.ca.gov
Dr. Michael Johnson	University of California, Davis	Contractor Project Manager	Ph: (530) 752-8837 Fax: (530) 297-4684 mbjohnson@ucdavis.edu
Melissa Turner	University of California, Davis	Contractor QA Officer	Ph: (530) 297-4684 Fax: (530) 297-4684 mmturner@ucdavis.edu
Henry Calanchini	University of California, Davis	Contractor Project Supervisor	Ph: (530) 297-4684 Fax: (530) 297-4684 hjcalanchini@ucdavis.edu
Loc Nguyen	California Department of Fish and Game Water Pollution Control Laboratory	CDFG QA Officer	Ph: (916) 358-0314 Fax: (916) 985-4301 Lnguyen@ospr.dfg.ca.gov

Name	Organizational Affiliation	Title	Contact Information
Dave Crane	California Department of Fish and Game Water Pollution Control Laboratory	CDFG Lab Contract Manager	Ph: (916) 358-2859 Fax: (916) 985-4301 dcrane@ospr.dfg.ca.gov
Petra Lee	CVRWQCB	Regional Board Project Manager	(916) 464-4603 Fax: (916) 464-4779 plee@waterboards.ca.gov
Leticia Valadez	CVRWQCB	Regional Board QA Officer	Ph: (916) 464-4634 Fax: (916) 464-4782 LValadez@waterboards.ca.gov

4.2 Personnel Responsibilities

Contract Manager role:
Jay Rowan is the Contract Manager. Jay Rowan is responsible for obtaining all services and analytical results/reports from the CDFG Lab Manager and all services and reports generated by the AEAL.

Contractor Project Manager role:
Michael Johnson is the UC Davis Project Manager. He will be responsible for all aspects of the project including the organization of field staff, scheduling of sampling days and interactions with the CDFG laboratory and the CVRWQCB.

AEAL Quality Assurance Officer role:
Melissa Turner is the AEAL Quality Assurance Officer. Melissa Turner's role is to establish the quality assurance and quality control procedures found in this QAPP as part of the sampling and field analysis procedures. Melissa Turner will also work with Loc Nguyen, the Quality Assurance Officer for CDFG Laboratory, by communicating all quality assurance and quality control issues contained in this QAPP to the CDFG Laboratory.

Contractor Project Supervisor role:
Henry Calanchini is the Project Supervisor. The project supervisor will assist the project manager by hiring, training, and supervising all monitoring staff, and summarizing all data into reports and submitting to the CVRWQCB along with copies of all raw data. The project supervisor will be responsible for monitoring spray application and weather conditions and in coordination with the Regional Board project manager, will determine when to begin sampling each storm event.

CDFG Quality Assurance Officer role:
Loc Nguyen is the CDFG Quality Assurance Officer. Loc will maintain all records associated with the receipt and analysis of samples analyzed for organophosphate pesticides, and will verify that the measurement process was "in control" (i.e., all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch.

CDFG Quality Lab Contract Manager role:
Dave Crane is the CDFG Lab Contract Manager. Dave will oversee the actions of all persons at CDFG involved with handling and analyzing project samples and reporting sample data. Dave is responsible for maintaining all project records and data generated at the CDFG lab. Dave will handle all CDFG contracting and budgetary responsibilities as they relate to the project.

Regional Board Project Manager role:
Petra Lee is the Regional Board Project Manager for this project. Petra will oversee the actions of all persons maintaining records and data as well as maintain a final, approved copy of the QAPP (including any changes and updates). She will also determine the sampling sites, frequency, and time periods and oversee budgetary expenses related to this monitoring study.

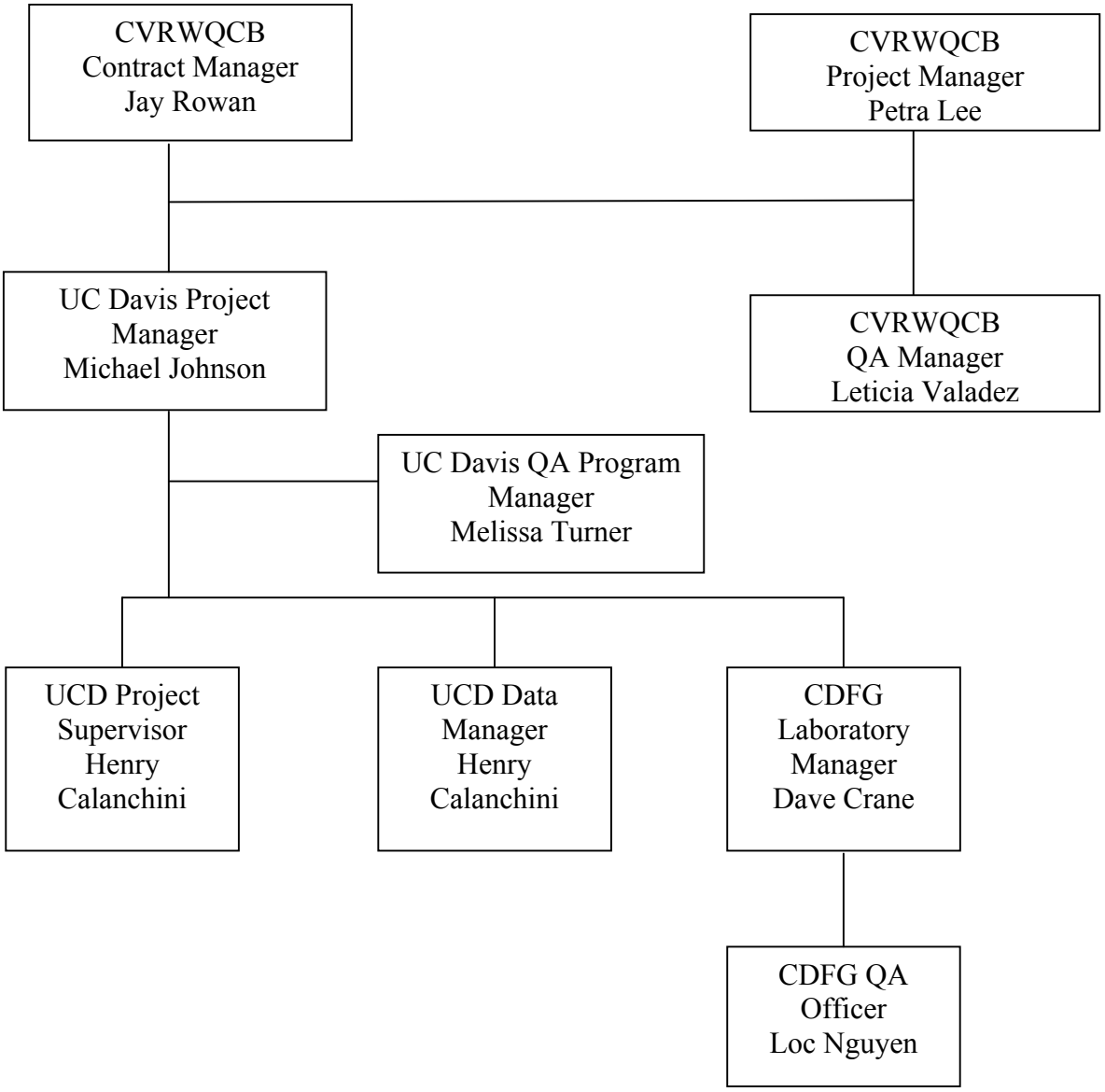
Regional Board Project QA Officer role:
Leticia Valadez is the Regional Board Quality Assurance Officer. Leticia will be responsible for verifying that the quality assurance and quality control procedures found in this QAPP meet the standards developed for Surface Water Ambient Monitoring Program (SWAMP) QAPPs as set forth in the Electronic Template for SWAMP-Compatible Quality Assurance Project Plans (Nichol and Reyes, 2004). The Regional Board QA Officer will operate independently from the project contractors (AEAL and CDFG).

4.3 Persons responsible for QAPP update and maintenance.

Changes and updates to this QAPP may be made after a review of the evidence for change by CVRWQCB's Project Manager and Quality Assurance Officer, and with the concurrence of the Regional Board's Contract Manager. The AEAL QA Officer will be responsible for making the changes, submitting drafts for review, preparing a final copy, and submitting the final for signature.

4.4 Organizational chart and responsibilities

Figure 1. Organizational chart.



5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem statement.

Pesticides are applied to orchards and field crops throughout the year to control a variety of insect pests and weeds. Pesticides are washed into rivers and tributaries by winter rains and by irrigation runoff. Pesticide concentrations in the rivers and tributaries are often toxic to aquatic invertebrates. Aquatic invertebrates are the primary source of food for larval fish. Pesticide concentrations have exceeded California Department of Fish and Game (CDFG) water quality criteria that are designed to protect aquatic invertebrates.

5.2 Decisions or outcomes.

This project will provide information about levels of organophosphate pesticides and other selected pesticides in water bodies of the Sacramento River basin, the eastern Sacramento-San Joaquin Delta tributary area (Delta), and the San Joaquin River basin through the collection and analysis of water samples. This information will be used to further characterize and define the sources of diazinon, chlorpyrifos and other pesticides that cause surface water contamination and toxic conditions to aquatic life. The results of this study will be used to support the development and implementation of pesticide Total Maximum Daily Loads (TMDL's) in Central Valley waterways and to characterize the presence/absence, sources, and usage patterns of selected other pesticides that have been identified as posing a high risk to surface waters.

5.3 Water quality or regulatory criteria

According to USEPA guidelines, aquatic organisms should not be affected unacceptably if the four-day average concentration of a pesticide does not exceed the pesticide's Criterion Continuous Concentration (CCC) value and if the one-hour average concentration does not exceed the Criteria Maximum Concentration (CMC) value more than once every three years on the average. The California Department of Fish and Game develops the CMC and CCC standards used in California surface waters.

The freshwater CMC and CCC values for diazinon in surface waters of the Sacramento River basin are 0.080 µg/L and 0.050 µg/L, respectively. In all other surface waters of the Central Valley the freshwater CMC and CCC values for diazinon are 0.160 µg/L and 0.100 µg/L, respectively. The freshwater CMC and CCC values for chlorpyrifos in all surface waters of the Central Valley are 0.025 µg/L and 0.014 µg/L, respectively. (Siepmann and Finlayson, 2000).

Table 1A. (Element 5) Water Quality Regulatory Criteria

Analyte	CMC (ppb)	CCC (ppb)	FAV (ppb)	FAB (ppb)
Chlorpyrifos	0.020	0.014		
Diazinon	0.080	0.050		
Azinphos methyl				
Malathion	0.430			
Methidathion				
Methyl parathion			0.170	0.080
Paraquat dichloride				
Diuron				
Carbofuran			1.500	0.500
Carbaryl	2.500	2.500		
Methiocarb				
Aldicarb				
Captan				

Analyte	CMC (ppb)	CCC (ppb)	FAV (ppb)	FAB (ppb)
Linuron				
Methomyl	5.500	0.520		
Propanil				
Propargite				
Oxyfluorfen				
Trifluralin				

Criterion maximum concentration (CMC) and criterion continuous concentration (CCC) values are reported for analytes which were issued under 1985 EPA aquatic-life criteria and represent a 1-hour average and a 4-day average, repectively. Analytes for which criteria were issued under the 1980 EPA aquatic-life criteria are reported as final acute value (FAV) and final chronic value (FCV), which represent an instantaneous value and a 24-hour average, respectively. Analytes with blank fields in all columns have insufficient toxicity data to compute criteria.

This Page Intentionally Left Blank

6. PROJECT/TASK DESCRIPTION

6.1 Work statement and produced products.

This project will monitor concentrations of diazinon, chlorpyrifos and other pesticides, and water pH, electrical conductivity and temperature at 20 waterway sites in the Sacramento Basin and the Delta for up to eight consecutive days during two winter storms and once a week or once every two weeks during the irrigation months of March-April and July. Locations for pesticide monitoring were selected on the basis of documented use of these pesticides upstream from the locations monitored, on pesticide-caused toxicity detected at these streams/rivers, and on inclusion of target pesticides on the 303(d) list of impaired water bodies. Data obtained will be used to quantify ambient levels of pesticides in the Sacramento and Delta watersheds and in the development of TMDLs for tributaries within the Sacramento basin and Delta.

Two data reports will be written; one for the storm season monitoring and one for the irrigation season monitoring. The final data reports will summarize the activities conducted to generate that data – including sample collection, storage and analysis. The data reports will contain, as an appendix, a CD containing, in tabular format, all data generated during this project, as well as the diazinon and chlorpyrifos load estimates for the two Sacramento River sites. The report will also include the results of the analysis of QC samples and an assessment of the overall quality of the data generated in comparison to the goals described in the QAPP. A preliminary draft of the storm season and TMDL compliance monitoring data report should be submitted to the CVRWQCB by May 1, 2006. A preliminary draft of the irrigation season data report should be submitted to the CVRWQCB by October 1, 2006. Following a review period of no longer than two weeks, Regional Board staff will submit any comments they have on the preliminary drafts. The storm season and TMDL compliance monitoring report will be finalized by June 15, 2006 and the irrigation season monitoring report will be finalized by November 15, 2006.

6.2. Constituents to be monitored and measurement techniques.

Concentrations of diazinon, chlorpyrifos and other pesticides will be determined with Gas Chromatography Flame Photometric Detector (GC-FPD), Gas Chromatography Mass Spectrometry/Mass Spectrometry. (GC-MSMS) and Liquid Chromatography-Mass Spectrometry (LC-MS). Copies of the methods are attached as appendices and a demonstration of performance is available at the CDFGs Water Pollution Control Laboratory.

Monitoring will also consist of field measurements for pH, conductivity and temperature using Oakton pH/Con 10 pH/Conductivity/Temperature meters.

6.3 Project schedule

Table 2. (Element 6) Project schedule timeline.

Activity	Date (MM/DD/YY)		Deliverable	Deliverable Due Date
	Anticipated Date of Initiation	Anticipated Date of Completion		
Dormant spray monitoring	12/10/2005	3/1/2006	none	NA
Winter storm sample collection	1/3/2006	3/20/2006	Sample concentration data	Within 4 weeks of sample delivery
Summarize winter storm sampling data	3/1/2006	4/22/2006	Complete data set	5/2/2006
Draft report of winter sampling	3/20/2006	5/1/2006	Draft final report for review	5/1/2006
Final report of winter sampling	5/16/2006	6/15/2006	Final report	6/15/2006
Spring irrigation season sample collection	3/7/2006	4/25/2006	Sample concentration data	Within 4 weeks of sample delivery
Summer irrigation season sample collection	7/6/2006	7/27/2006	Sample concentration data	Within 4 weeks of sample delivery
Summarize all irrigation sampling data	4/7/2006	9/1/2006	Complete data set	9/1/2006
Draft report of all irrigation sampling	7/27/2006	10/1/2006	Draft final report for review	10/1/2006
Final report of all irrigation sampling	5/16/2006	11/15/2006	Final report	11/15/2006

6.4 Geographical setting

The sampling area encompasses the lower Sacramento River basin to the north (Figures 2, 3a), the eastern Sacramento-San Joaquin Delta tributary area to the south (Figure 3b), and the San Joaquin River basin to the south (Figure 4).

Figure 2. Five TMDL monitoring sites in the Sacramento River Basin to be monitored for propanil during the 2006 rice irrigation season.

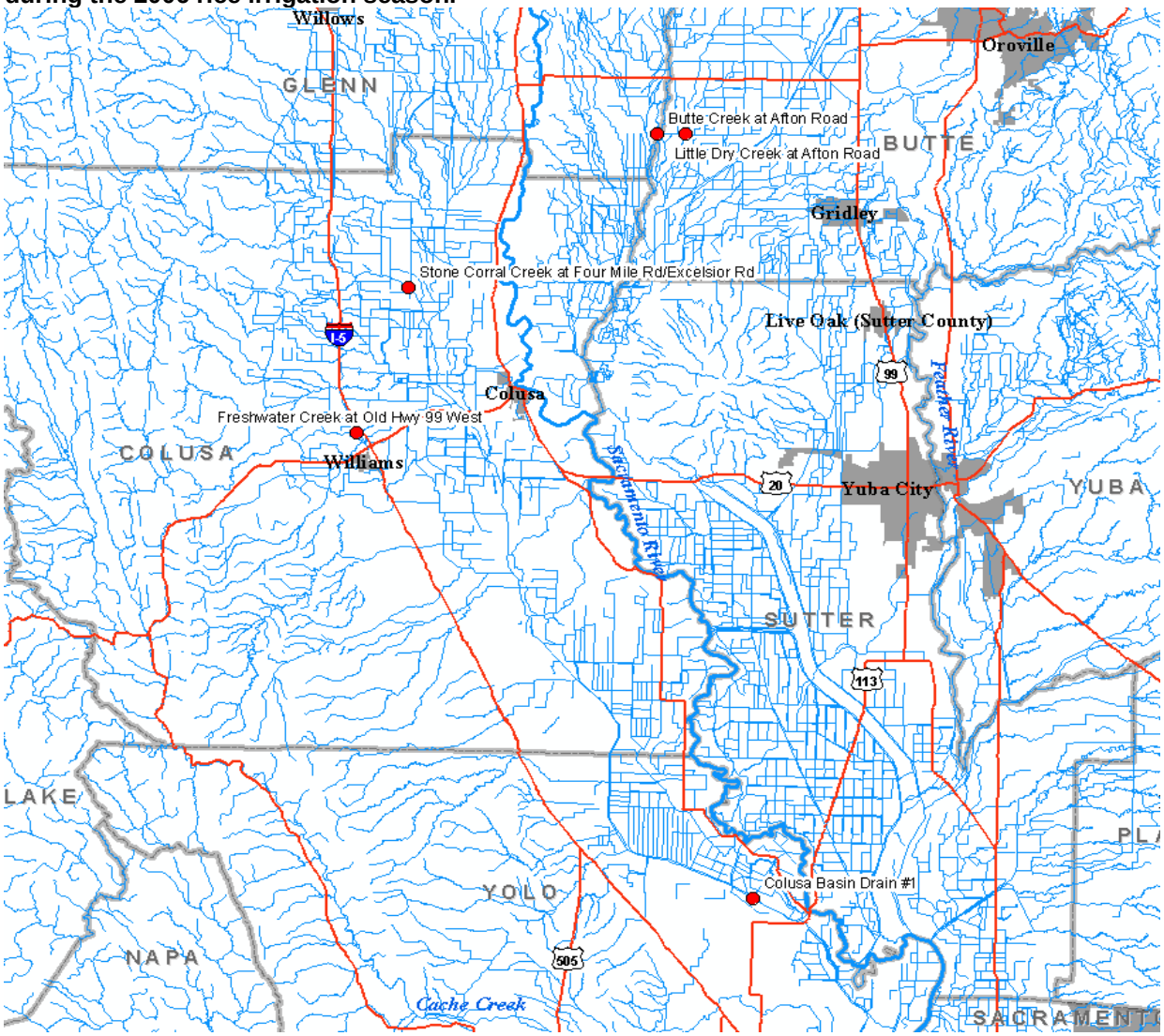


Figure 3a. Four TMDL monitoring sites in the Sacramento River Basin to be monitored for pesticides during the 2006 orchard dormant spray and spring-summer irrigation seasons.

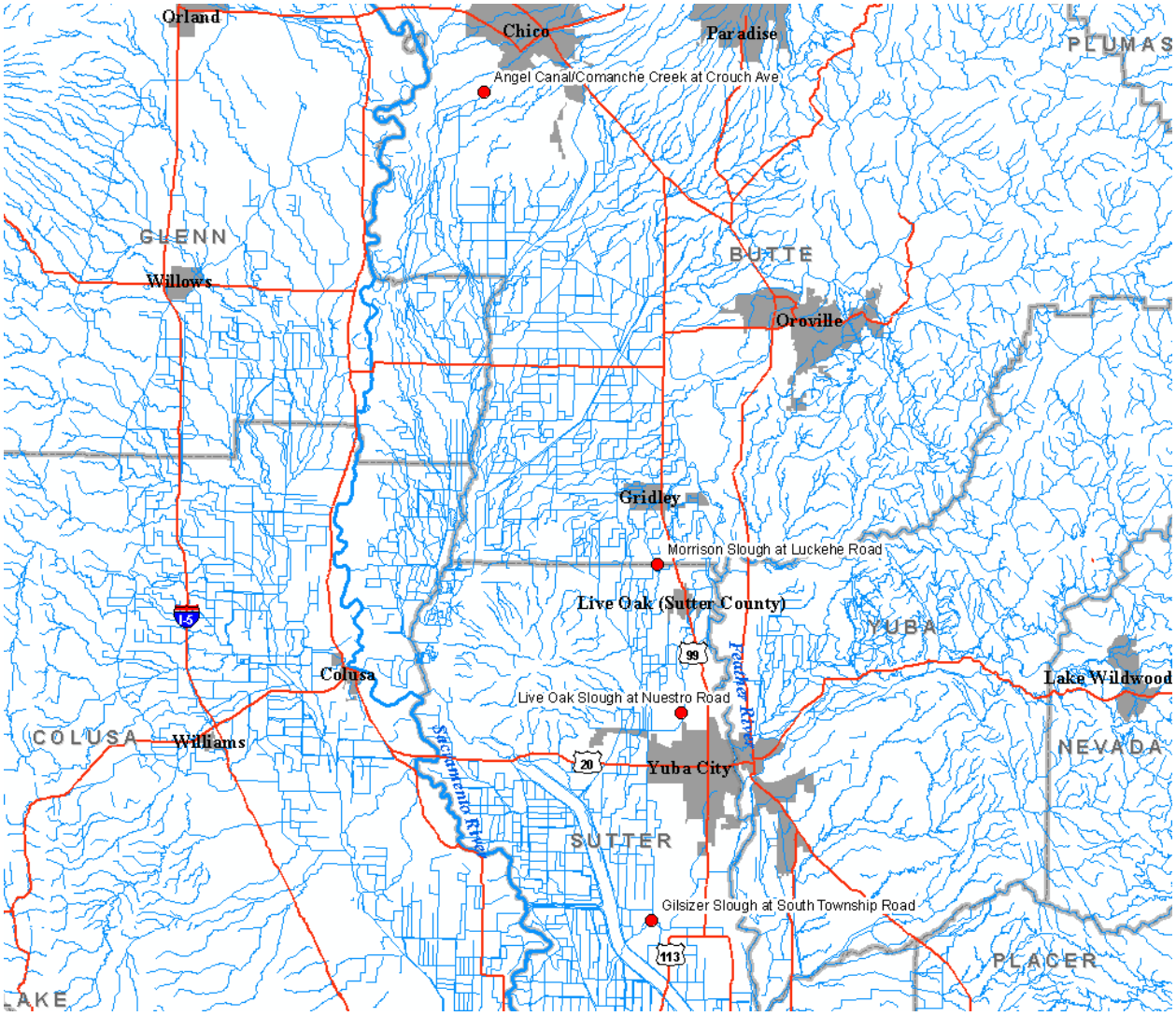


Figure 3b. Six TMDL monitoring sites in the Sacramento River Basin and Delta to be monitored for pesticides during the 2006 orchard dormant spray and spring-summer irrigation seasons.

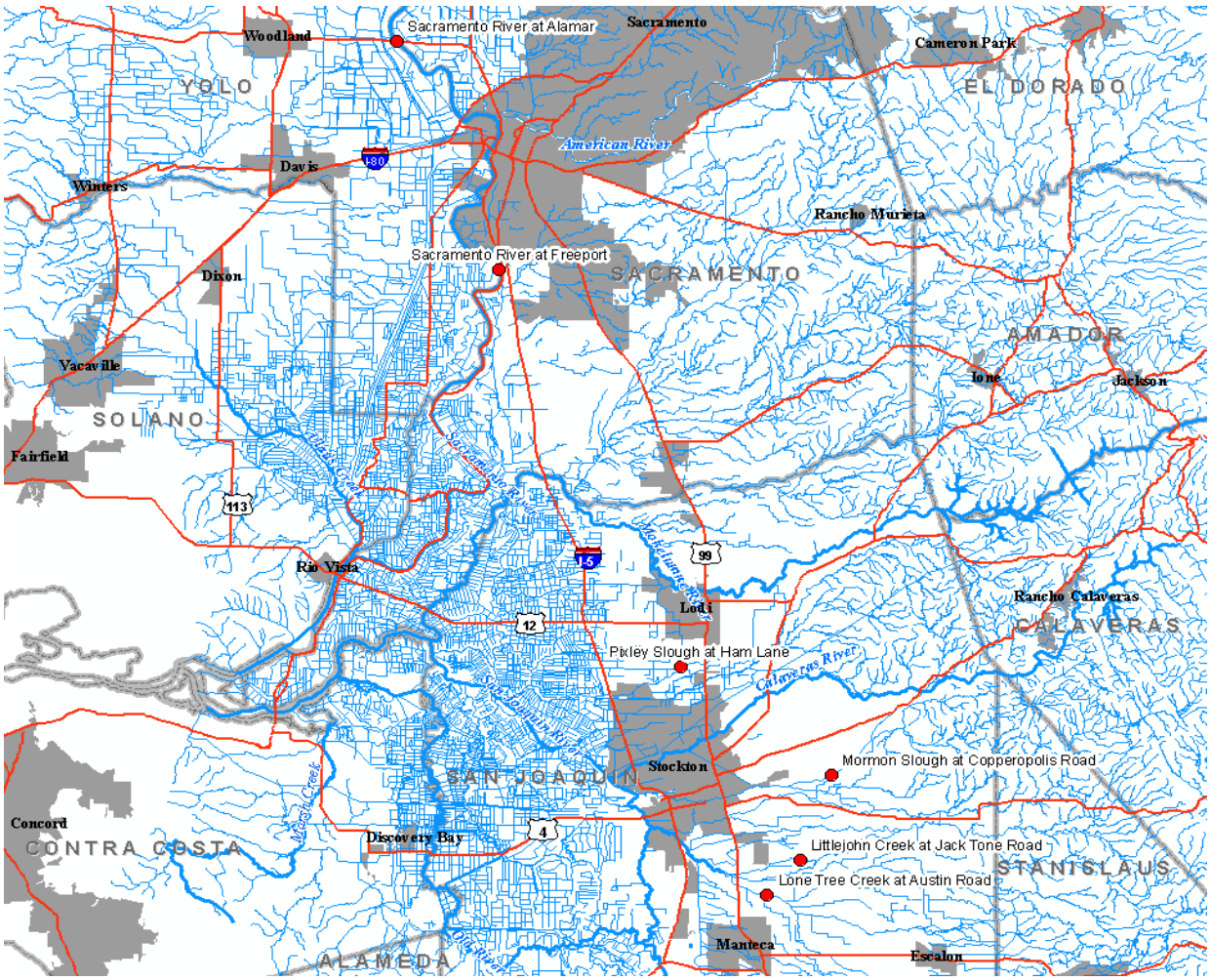
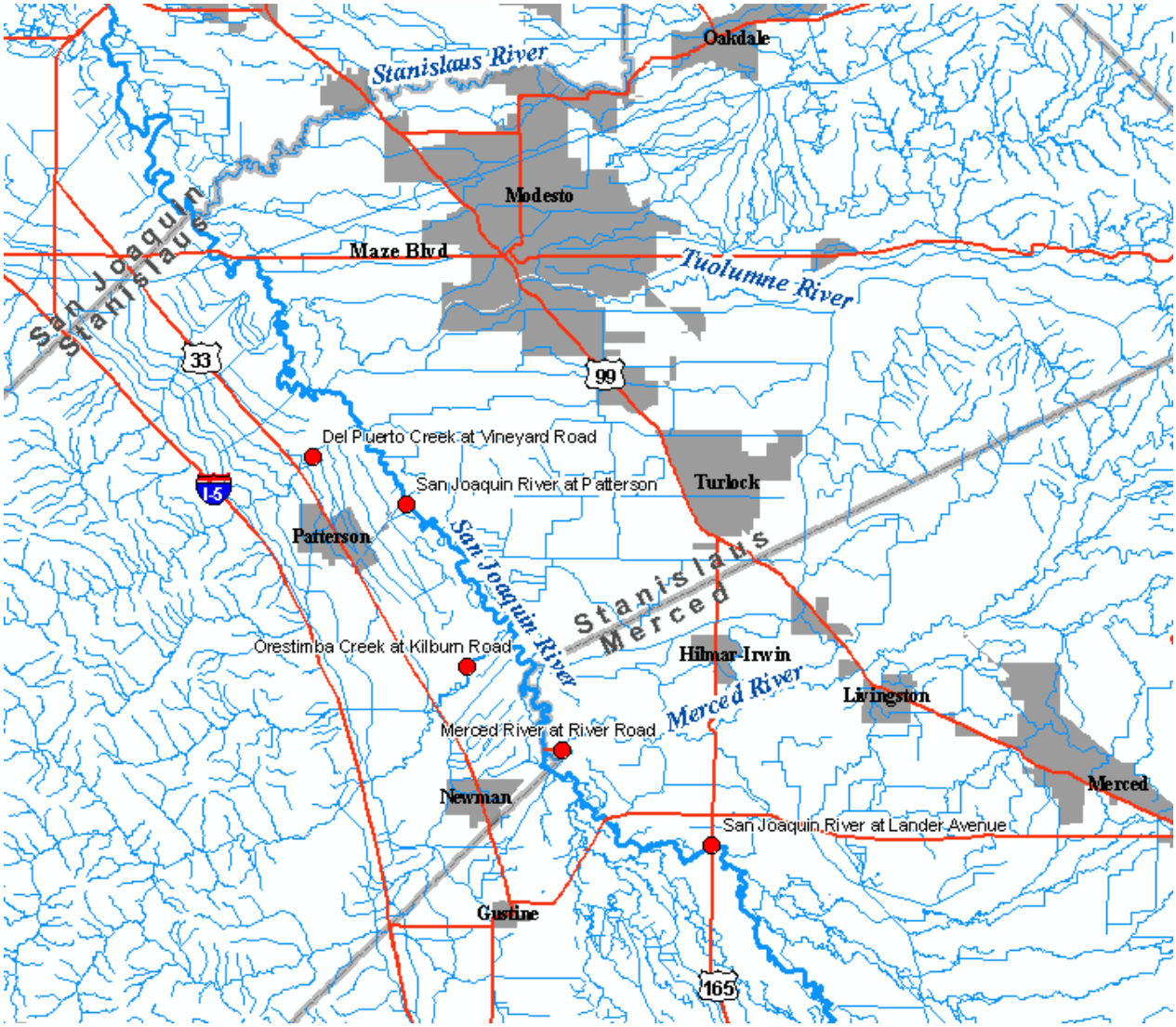


Figure 4. Five TMDL monitoring sites in the northern San Joaquin River Basin to be monitored for pesticides during the 2006 orchard dormant spray and spring-summer irrigation seasons.



6.5 Constraints

Calculated loads of pesticides are based on the collection of 1-2 samples per day at each site and therefore, are only a best estimate of what is actually moving through each system based on a limited number of samples. Storm intensity and duration affect the rate of pesticide runoff. In extreme wet weather conditions runoff of pesticides may occur so rapidly that accurate estimates of pesticide loads are not possible to obtain.

This Page Intentionally Blank

7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Field and Laboratory Measurements Data Quality Objectives Tables

Table 3. (Element 7) Data quality objectives for field measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limit	Completeness
Field Testing	Temperature	± 0.5 °C	± 0.5 °C	NA	NA	90%
	Electrical Conductivity	± 5%	± 5%	NA	NA	90%
	pH	± 0.5 units	± 0.5 units	NA	NA	90%

Table 4. (Element 7) Data quality objectives for laboratory measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
Organophosphates	Diazinon	MS/MSD 70%-125% Lab Control Spike 70%-125%	Field replicate or MS/MSD ± 25% RPD. Field replicate minimum.	MS/MSD 70%-125% Lab Control Spike 70%-125%	0.005 ppb	90%
Organophosphates	Chlorpyrifos	same	same	same	0.005 ppb	90%
Organophosphates	Azinphos methyl	same	same	same	0.050 ppb	90%
Organophosphates	Malathion	same	same	same	0.050 ppb	90%
Organophosphates	Methidathion	same	same	same	0.050 ppb	90%
Organophosphates	Methyl parathion	same	same	same	0.050 ppb	90%
Carbamates	diuron	same	same	same	0.005 ppb	90%
Carbamates	carbofuran	same	same	same	0.020 ppb	90%
Carbamates	carbaryl	same	same	same	0.020 ppb	90%
Carbamates	methiocarb	same	same	same	0.250 ppb	90%
Carbamates	aldicarb	same	same	same	0.050 ppb	90%
Carbamates	captan	same	same	same	0.100 ppb	90%
Carbamates	linuron	same	same	same	0.005 ppb	90%
Carbamates	methomyl	same	same	same	0.020 ppb	90%
Herbicides	propanil	same	same	same	0.100 ppb	90%
Herbicides	propargite	same	same	same	0.500 ppb	90%
Herbicides	oxyfluorfen	same	same	same	0.050 ppb	90%
Herbicides	trifluralin	same	same	same	0.100 ppb	90%
Herbicides	Paraquat dichloride	same	same	same	0.050 ppb	90%

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Specialized training or certifications.

All staff performing field or laboratory procedures shall receive training from the AEAL Quality Assurance Officer, Melissa Turner, to ensure that the work is conducted correctly and safely. At a minimum, all staff shall be familiar with the field guidelines and procedures and the laboratory SOP included in this QAPP. All staff/students conducting fieldwork must have completed the Field Safety Training course administered by the AEAL and the Drivers Safety Training Course administered by UC Davis. All work shall be performed under the supervision of experienced staff or a field coordinator. A copy of the staffs' training records will be filed in each specific project file.

8.2 Training and certification documentation.

Field staff training is documented and filed in the UC Davis Aquatic Ecosystems Analysis Laboratory (AEAL) office in Davis, CA. Documentation consists of a record of the training date, instructor, whether initial or refresher, and whether the course was completed satisfactorily.

AEAL maintains records of its training. Those records can be obtained if needed from the AEAL Quality Assurance Officer, Melissa Turner.

8.3 Training personnel.

All project staff will attend the Field Safety Training Course taught by Henry Calanchini and Anja Wehrmann on December 22 at the AEAL office in Davis, CA. A representative of the UC Davis Fleet Services will teach the Drivers Safety Training Course to all project staff on December 20 in the AEAL office in Davis, CA.

Table 5. (Element 8) Specialized personnel training or certification.

Specialized Training Course Title or Description	Training Provider	Personnel Receiving Training/ Organizational Affiliation	Location of Records & Certificates
Field Safety Training	Henry Calanchini Anja Wehrmann AEAL	All UCD and SWRCB sampling staff	AEAL office
Drivers Safety Training	Bob Jahn, UC Davis	All UCD and SWRCB sampling staff	AEAL office

9. DOCUMENTS AND RECORDS

AEAL will collect records of sample collection, field analyses, and laboratory analysis. Samples sent to the CDFG Water Pollution Control Laboratory will include a Chain of Custody (COC) form. AEAL generates records for sample receipt and storage, analyses, and reporting.

AEAL has an existing database of field measurements from previous studies. The Project Supervisor, Henry Calanchini, maintains this database. Mr. Calanchini will also maintain the database of information collected in this project.

All records generated by this project will be stored at AEAL's main office. CDFG records pertinent to this project will be maintained at CDFG's main office. Copies of all records held by CDFG will be provided to AEAL and stored in the project file.

Copies of this QAPP will be distributed to all parties involved with the project, including field collectors and the AEAL in-house laboratory analyst. Copies will be sent to the CDFG Manager for distribution within the CDFG. Any future amended QAPPs will be held and distributed in the same fashion. All originals, and subsequent amended QAPPs, will be held at the CVRWQCB. Copies of versions, other than the most current, will be discarded so as not to create confusion.

Persons responsible for maintaining records for this project are as follows. Henry Calanchini, Project Supervisor will maintain all sample collection, sample transport, chain of custody, and field analyses forms. Dave Crane, CDFG laboratory manager will maintain all records associated with the receipt and analysis of samples analyzed for pesticides. Henry Calanchini will maintain the database; data management procedures including back-up plans for data stored electronically are outlined in Element 19 of this QAPP. Dave Crane will maintain CDFG's records. CVRWQCB Project Manager Petra Lee will oversee the actions of these persons and will arbitrate any issues relative to records retention and any decisions to discard records.

All records will be passed to the Regional Board Project Manager, Petra Lee, at project completion. Copies of the records will be maintained at AEAL and CDFG for five years after project completion then discarded, except for the database, which will be maintained without discarding.

Two data reports will be made; one each for the storm season monitoring and the irrigation season monitoring. The final data reports will summarize the activities conducted to generate that data – including sample collection, storage and analysis. The data reports will contain, as an appendix, a CD containing, in tabular format, all data generated during this project, as well as the diazinon and chlorpyrifos load estimates for the two Sacramento River sites. The report will also include the results of the analysis of QC samples and an assessment of the overall quality of the data generated in comparison to the goals described in the QAPP. A preliminary draft of the storm season and TMDL compliance monitoring data report should be submitted to the CVRWQCB by May 1, 2006. A preliminary draft of the irrigation season data report should be submitted to the CVRWQCB by October 1, 2006. Following a review period of no longer than two weeks, Regional Board staff will submit any comments they have on the preliminary drafts. The storm season and TMDL compliance monitoring report will be finalized by June 15, 2006 and the irrigation season monitoring report will be finalized by November 15, 2006.

Table 6. (Element 9) Document and record retention, archival, and disposition information.

	Identify Type Needed	Retention	Archival	Disposition
Sample Collection Records	Chain of Custody	Original with CDFG	Copies with AEAL and CVRWQCB	Stored at the Regional Board for at least 5 years
Field Records	Field Data Sheet	AEAL	AEAL	Stored at AEAL for 5 years
Analytical Records	Excel Sample Reports	CDFG	Copies to AEAL and CVRWQCB	Stored at the Regional Board for at least 5 years
Data Records	Excel database	AEAL	Copy to CVRWQCB	Stored at the Regional Board for at least 5 years
Assessment Records	Draft and Final Data Reports	AEAL	Copy to CVRWQCB	Stored Permanently at Regional Board

GROUP B: DATA GENERATION AND ACQUISITION

10. SAMPLING PROCESS DESIGN

All information generated in this study is considered to be critical to project success. Sampling sites and locations are listed in the monitoring plan (Appendix 1). In general, sampling locations were selected throughout Region 5. Locations for pesticide monitoring (other than the two Sacramento River sites) were selected by Regional Board staff on the basis of documented use of organophosphates, carbamates and herbicides upstream from the locations monitored, on pesticide-caused toxicity detected in these streams/rivers, and on inclusion of target pesticides on the 303(d) list of impaired water bodies.

The two sites on the Sacramento River were selected to assess progress in meeting the water quality objectives for diazinon in the Sacramento River, and the load allocations set in the Sacramento and Feather River diazinon TMDL for the Colusa Basin, and the discharges into the Sacramento River Between Alamar and Freeport. The Sacramento Valley Water Quality Coalition will monitor other Sacramento and Feather River diazinon TMDL compliance sites.

For the "high risk" pesticide monitoring, target pesticides were identified from a report drafted by the CVRWQCB titled *Relative Risk Evaluation for Pesticides Used in the Sacramento River Watershed* (Lu 2005). The report considered the following factors to evaluate and rank the overall relative risk of each target pesticide to impact surface water: "toxicity to aquatic organisms; and chemical and physical properties - mainly water solubility, soil absorption coefficient (Koc), and half-life in soil" (Lu 2005). The table of highest risk pesticides was selected from the report. Priority pesticides were then selected from the highest risk group using the following criteria:

- Rice pesticides that have regulatory action were eliminated leaving only propanil.
- Pyrethroids were eliminated due to their strong hydrophobic nature making them difficult to capture in the water column.
- Organophosphates and any pesticide for which use is decreasing were eliminated.

- Pesticides with relatively high Koc values were eliminated due to their propensity to quickly move out of the water column and in to soil. Paraquat was an exception due to its high solubility.
- Pesticides having a relatively short half-life were eliminated because they are less likely to be captured in runoff.

Sites to be monitored for "high risk" pesticides were selected using the following process:

- The most recent (2003) Pesticide Use Report (PUR) data was obtained from the California Department of Pesticide Regulation and transferred into a graphical format using GIS to show pounds of active ingredient use per section for each pesticide of interest.
- Maps were used to locate potential sampling sites near or slightly downstream of pesticide applications.
- All potential sites were checked against existing monitoring sites of other projects, groups or agencies in order not to duplicate sampling efforts.
- The relative risk report was used to determine seasonal timing of "high risk" pesticide applications.
- Monitoring schedules were constructed, using the temporal and spatial pesticide data, to maximize the potential of capturing pesticide runoff.

In the event that a site becomes inaccessible or unsafe to sample for any reason an alternative sampling site for the affected water body will be scouted by sampling personnel. Sampling personnel will notify the AEAL Project Supervisor of the alternative site and any conditions that may influence the quality of a sample collected at the site. The AEAL Project Supervisor will then seek permission from the Regional Board Project Manager to collect a sample at the alternative site.

If for any reason a regularly scheduled sample cannot be collected the sampling crew will notify the Regional Board Project Manager of the problem and seek approval to collect the sample on the next possible day. Should the postponed sample coincide with the next sampling event, the sampling will be extended by the time period in which the sample was missed. For example, if one day of storm sampling was missed, a sample will be collected for one additional day during the next sampling event. If a weekly sample was missed, the sampling schedule will be extended one week so that the total numbers of samples in the original sampling schedule are collected.

Because the sampling sites are in predetermined locations and the sampling personnel are assigned specific sites for the duration of this project, the natural variability of the sampling process is limited to the time at which the samples are collected and localized soil conditions and weather patterns. The concentration of target pesticides will fluctuate on a temporal basis at each sampling site depending upon the rate at which pesticide runoff occurs, the amount of pesticide entering the subject water body, distance the pesticide has traveled from its source, the speed at which it travels, and the volume of water passing by that point. The saturation level of soils affects the rate of pesticide runoff. More rainfall is required to generate runoff when soil conditions are dry than when soil has been saturated from previous rainfall or irrigation. Localized weather patterns affect the rate of pesticide runoff with heavy rainfall generating faster runoff than light rain.

Factors that could bias contaminant levels found in the samples include poor sampling techniques and improper cleaning of equipment as well as limited access to parts of the channel. These sources of bias can be avoided through strict adherence to the methods described in Element 11and Appendices 3, 4, and 5.

11. SAMPLING METHODS

At sites where a bridge is present and pedestrian access is available, samples will be collected by lowering a 3L Teflon® bottle in a weighted cage at three[1] equally spaced intervals across the width of the stream channel. At each vertical the bottle will be filled ¼ full. After collecting the three verticals the 3L bottle will be capped, agitated to ensure thorough mixing, and poured into a pre-labeled 1L amber glass bottle. The 3L bottle will be cleaned after each sample in accordance with the methods outlined in Appendix 3: Surface Water Sample Collection SOP.

[1] At the Freeport Bridge the sample will consist of a single vertical due to limited pedestrian access.

At all other sites grab samples will be collected using a pole sampler from as near to the center of the channel as possible. Regardless of collection method, all samples will be poured into Fisher Scientific 300 Series certified pre-cleaned 1L amber glass bottles. The bottles will be filled so that no headspace remains prior to capping. All samples will be immediately placed on ice, in coolers, and preserved at 4° C until delivery to the CDFG lab.

Table 7. (Element 11) Sampling locations and sampling methods.

Sampling Location	Location ID Number	Matrix	Analytical Parameter	# Samples (incl. field duplicates, field blanks, and matrix spikes)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
Sacramento River at Alamar	519LSAC55	Water	Organophosphates pesticides	9	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Sacramento River at Freeport	519LSAC52	Water	Organophosphate pesticides	9	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Gilsizer Slough at South Township Road	520LSAC23	Water	Organophosphates Carbamates Herbicides	27	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Live Oak Slough at Nuestro Road north of Yuba City	520LSAC24	Water	Organophosphates Carbamates Herbicides	27	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Morrison Slough at Luckehe Road near Live Oak	520LSAC25	Water	Organophosphates Carbamates Herbicides	27	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Angel Canal/Comanche Creek at Crouch Avenue	520LSAC26	Water	Organophosphates Carbamates Herbicides	27	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Pixley Slough at Ham Lane	531DEL501	Water	Organophosphates Carbamates Herbicides	24	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Mormon Slough at Copperopolis	531DEL502	Water	Organophosphates Carbamates Herbicides	28	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days

Sampling Location	Location ID Number	Matrix	Analytical Parameter	# Samples (incl. field duplicates, field blanks, and matrix spikes)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
Littlejohn Creek at Jack Tone Road	531DEL503	Water	Organophosphates Carbamates Herbicides	27	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Lone Tree Creek at Austin Road	531SJC503	Water	Organophosphates Carbamates Herbicides	31	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Little Dry Creek at Afton Road	520LSAC27	Water	Propanil	9	Appendix 3	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Butte Creek at Afton Road	520LSAC28	Water	Propanil	9	Appendix 3	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Stone Corral Creek at Four Mile Road/Excelsior Road (near Maxwell)	520LSAC29	Water	Propanil	9	Appendix 3	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Freshwater Creek at Old Hwy 99 West (near Williams)	520LSAC30	Water	Propanil	9	Appendix 3	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Colusa Basin Drain #1	520LSAC31	Water	Propanil	9	Appendix 3	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
San Joaquin River at Patterson	541STC507	Water	Carbamates Herbicides	7	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
San Joaquin River at Lander	541MER522	Water	Carbamates Herbicides	8	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days

Sampling Location	Location ID Number	Matrix	Analytical Parameter	# Samples (incl. field duplicates, field blanks, and matrix spikes)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
Merced River at River Road	535MER546	Water	Carbamates Herbicides	14	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Del Puerto Creek at Vineyard Road	541STC516	Water	Organophosphates Carbamates Herbicides	18	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Orestimba Creek at Kilburn Road	541STC518	Water	Organophosphates Carbamates Herbicides	18	Appendix 3	1L each group	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days

12. SAMPLE HANDLING CUSTODY

Once sample containers are filled, they are labeled and stored on ice for transport to the CDFG laboratory. Sample containers will be Fisher Scientific 300 Series certified pre-cleaned 1L amber glass bottles.

Environmental samples are delivered to the CDFG lab on the day of collection or the following day. If samples are to be delivered the following day they will be kept in a secure space at the AEAL.

Samples may be kept at 4° C, in the dark, for up to 7 days. Extraction must be performed within 7 days of the time of sample collection; analysis must occur within 40 days of extraction (USEPA SW846).

Table 8. (Element 12) Sample handling and custody.

Parameter	Container	Volume	Initial Preservation	Holding Time
Selected organophosphate pesticides	Fisher Scientific 300 Series amber	1L	ice	7 days
selected carbamate pesticides	Fisher Scientific 300 Series amber glass bottle	1L	ice	7 days
paraquat dichloride	Fisher Scientific 300 Series amber glass bottle	1L	ice	7 days
selected herbicides	Fisher Scientific 300 Series amber glass bottle	1L	ice	7 days

No special handling or custody procedures are needed. The chain of custody form is used as a shipping record.

Samples may be disposed of when analysis completed and all analytical quality assurance/quality control procedures are reviewed and accepted

Each sample will be documented on a chain of custody form at the time of collection. The chain of custody will remain with the samples at all times. When the samples are delivered to the lab the sampler will relinquish custody by signing the appropriate space on the chain of custody form. The lab attendant will accept custody by signing the appropriate space on the chain of custody form. The lab attendant will make a copy of the chain of custody form and give it to the sampler for filing at the AEAL office.

The following page contains an example of a TMDL monitoring chain of custody form

DFG REQUEST FOR ANALYSIS AND CHAIN OF CUSTODY RECORD

Page_____ of _____

Sampler	**Send Results To** Petra Lee plee@waterboards.ca.gov	**Lab Number**
Address UC Davis 1490 Drew Ave Suite 150	Henry Calanchini hjcalanchini@ucdavis.edu	**Field Number**
City Davis **Zip** 95616 **CA**		**Lab Storage**

Ice Chest Temp at Log-in:	**Analysis Requested>>>**		Organophosphates	Paraquat dichloride	Carbamates	Herbicides									Others (specify)			# of containers			
	Collection																				
Sample Identification	**Date**	**Time**																**Plastic**	**Glass**	**Vial**	**Whirlpak**

Comments / Special Instructions

Samples Reliquished By (Signature)	**Print Name**	**Date**	**Received By** (Signature)	**Print Name**	**Date**

This Page Intentionally Blank

13. ANALYTICAL METHODS

See Tables 9 and 10 for analytical methods. When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for all parameters of interest. See methods listed in Appendices 6-9 for specific analytical procedures. It is the responsibility of the analytical chemist to follow these procedures, take any necessary corrective actions, and document all procedures and actions taken.

Table 9. (Element 13) Field analytical methods.

Analyte	Laboratory / Organization	Project Action Limit	Project Quantitation Limit	Analytical Method		Achievable Laboratory Limits	
				Analytical Method/ SOP	Modified for Method yes/no	MDLs†	Method
pH	Field monitoring by AEAL field staff	NA	±0.01 pH	Appendix 5	None	NA	NA
Conductivity	Field monitoring by AEAL field staff	NA	0.01 mS	Appendix 5	None	NA	NA
Temperature	Field monitoring by AEAL field staff	NA	0.1ºC	Appendix 5	None	NA	NA

(*) *Standard Methods for the Examination of Water and Wastewater*, 20th edition.
† MDL = Method Detection Levels

Table 10. (Element 13) Laboratory analytical methods.

Analyte	Laboratory/ Organization	Project Action Limit	Project Reporting Limit	Analytical Method		Achievable Laboratory Limits	
				Analytical Method/ SOP	Modified for Method yes/no	MDLs†	Method
Diazinon	CDFG	0.080 µg/L	0.020 µg/L	USEPA 8141A Appendix 6	No	0.003 µg/L	GC-FPD
Chlorpyrifos	CDFG	NA	0.010 µg/L	USEPA 8141A Appendix 6	No	0.003 µg/L	GC-FPD
Azinphos methyl	CDFG	NA	0.050 µg/L	USEPA 8141A Appendix 6	No	0.030 µg/L	GC-FPD
Malathion	CDFG	NA	0.050 µg/L	USEPA 8141A Appendix 6	No	0.030µg/L	GC-FPD
Methidathion	CDFG	NA	0.050 µg/L	USEPA 8141A Appendix 6	No	0.030 µg/L	GC-FPD

Analyte	Laboratory/ Organization	Project Action Limit	Project Reporting Limit	Analytical Method		Achievable Laboratory Limits	
				Analytical Method/ SOP	Modified for Method yes/no	MDLs†	Method
Methyl parathion	CDFG	NA	0.050 µg/L	USEPA 8141A Appendix 6	No	0.010 µg/L	GC-FPD
Paraquat dichloride	CDFG	NA	0.500 µg/L	USEPA 547 Appendix 8	Yes	0.200 µg/L	HPLC-MS
Diuron	CDFG	NA	0.005 µg/L	USEPA 632 Appendix 7	Yes	0.002 µg/L	HPLC-MS
Carbofuran	CDFG	NA	0.020 µg/L	USEPA 632 Appendix 7	Yes	0.010 µg/L	HPLC-MS
Carbaryl	CDFG	NA	0.020 µg/L	USEPA 632 Appendix 7	Yes	0.010 µg/L	HPLC-MS
Methiocarb	CDFG	NA	0.250 µg/L	USEPA 632 Appendix 7	Yes	0.150 µg/L	HPLC-MS
Aldicarb	CDFG	NA	0.050 µg/L	USEPA 632 Appendix 7	Yes	0.010 µg/L	HPLC-MS
Linuron	CDFG	NA	0.100 µg/L	USEPA 632 Appendix 7	Yes	0.050 µg/L	HPLC-MS
Captan	CDFG	NA	0.005 µg/L	USEPA 632 Appendix 7	Yes	0.002 µg/L	HPLC-MS
Methomyl	CDFG	NA	0.020 µg/L	USEPA 632 Appendix 7	Yes	0.010 µg/L	HPLC-MS
Propanil	CDFG	NA	0.100 µg/L	USEPA 619 Appendix 9	Yes	0.050 µg/L	GC-MSMS
Propargite	CDFG	NA	0.500 µg/L	USEPA 619 Appendix 9	Yes	0.200 µg/L	GC-MSMS
Oxyfluorfen	CDFG	NA	0.050 µg/L	USEPA 619 Appendix 9	Yes	0.020 µg/L	GC-MSMS
Trifluralin	CDFG	NA	0.100 µg/L	USEPA 619 Appendix 9	Yes	0.050 µg/L	GC-MSMS

† MDLs = Method Detection Limit

This Page Intentionally Blank

14. QUALITY CONTROL

Internal quality control (QC) is achieved by analyzing a series of duplicate, blank, spike, and spike duplicate samples to ensure that analytical results are within the specified QC objectives. The QC sample results are used to quantify precision and accuracy and identify any problem or limitation in the associated sample results. The internal QC components of a sampling and analyses program will ensure that the data of known quality are produced and documented. The quality control assessments used in the TMDL monitoring program are discussed below. Quality control acceptance limits and frequencies are summarized in Tables 11 and 12 and Appendix 2. Detailed procedures for preparation and analysis of quality control samples are provided in the analytical method document in Appendix 6.

14.1 Data Quality Objectives and Quality Assurance Objectives

Data Quality Objectives (DQOs) and Quality Assurance Objectives (QAOs) are related data quality planning and evaluation tools for all sampling and analysis activities. A consistent approach for developing and using these tools is necessary to ensure that enough data are produced and are of sufficient quality to make decisions for this study.

DQOs and Data Use Planning
DQOs specify the underlying reason for collection of data, data type, quality, quantity, and uses of data collection. For this program, data is needed for identification of sources and evaluation of management practices effectiveness.

Data Quality Category
Data will be analyzed using standard US Environmental Protection Agency (EPA) methods, or other reference methods approved by Regional Board staff. Data are analyte-specific. Each method has standardized Quality Control and documentation requirements that provide supporting information necessary to verify all reported results.

Quality Assurance Objectives (QAOs)

Quality assurance objectives are the detailed QC specifications for precision, accuracy, representativeness, comparability and completeness (PARC). The QAOs presented in this QAPP represent the minimum acceptable specifications that should be considered routinely for field and analytical procedures. The QAOs are then used as comparison criteria during data quality review by the Regional Board to determine if the minimum requirements have been met and the data may be used as planned.

14.2 Development of Precision and Accuracy Objectives

Laboratory control spikes (LCSs) are used to determine the precision and accuracy objectives. LCSs are fortified with target compounds to monitor the laboratory precision and accuracy.

Field duplicates measure sampling precision and variability for comparison of project data. Acceptable relative percent difference (RPD) is less than 25 for field duplicate analyses. If field duplicate sample results vary beyond these objectives, the results are further evaluated to identify the cause of the variability. The precision and accuracy objectives for this QAPP are listed in Table 4.

14.3 Precision Accuracy Representativeness Completeness (PARC) Definitions and Calculations

Precision
Precision measures the reproducibility of repetitive measurements. Precision is evaluated by calculating the RPD between duplicate spikes, duplicate sample analyses or field duplicate samples and comparing it with

appropriate precision objectives established in this QAPP. Analytical precision is developed using repeated analyses of identically prepared control samples. Field duplicate samples analyses results are used to measure the field QA and matrix precision. Interpretation of precision data must include all possible sources of variability. The precision objectives for this QAPP are listed in Table 4.

The **M**ean of the **A**bsolute value of single or aggregated **R**elative **P**ercent **D**ifference (MARPD) is used to express precision and is calculated as shown below:

$$MARPD = \frac{1}{k}\sum_{j=1}^{k}\left(\frac{|S1 - S2|}{S1 + S2}\right)_j \times 200$$

Where: S1 = The value for the primary sampler,
S2 = The value for the collocated sampler, and
k = The number of pairs of valid data.

For reporting purposes, the absolute value of the relative percent difference is used when a single pair is evaluated and referred to simply as ARPD or RPD. The formula shown above then reduces to:

$$RPD = \left(\frac{|S1 - S2|}{S1 + S2}\right) \times 200$$

Note: Signed results (positive and negative) are not generally used for reporting.

Accuracy

Accuracy measures correctness, or how close a measurement is to the true or expected value. Accuracy is measured by determining the percent recovery of known concentrations of analytes spiked into field sample or reagent water before extraction. The stated accuracy objectives for Laboratory control spikes or matrix spikes should reflect the Qualitative Objectives anticipated concentrations and/ or middle of the calibration range. The accuracy objectives for this QAPP are listed in Table 4. Accuracy can be calculated with the following formula:

$$\%R = \left[1 + \left(\frac{Y - X}{X}\right)\right] \times 100$$

Where: %R = Percent recovery. The amount measured as compared to the "true" value, expressed as a percentage,
Y = The measured value, and
X = The true value.

Representativeness

Representativeness is obtained by using standard sampling and analytical procedures listed and referenced in this QAPP to generate data that are representative of the sites.

Comparability

The comparability of data produced by and for this program is predetermined by the commitment of its staff and contracted laboratories to use standardized methods, where possible, including EPA-approved analytical

methods, or documented modifications thereof, which provide equal or better results. These methods have specified units in which the results are to be reported.

Measurements are made according to standard procedure, or documented modifications thereof which provide equal or better results, using common units such as Celsius, feet, feet/sec, mg/L, µg/L, mg/kg, etc. Analytical procedures are set by the USEPA approval list published in 40 CFR 136 (USEPA 2004(a)).

Completeness

Completeness is calculated for each method and matrix for an assigned group of samples. Completeness for a data set is defined as the percentage of unqualified and estimated results divided by the total number of the data points. This represents the usable data for data interpretation and decision-making. Completeness does not use results that are qualified as rejected or unusable, or that were not reported as sample loss or breakage. The overall objective for completeness is 90% for this project (Table 4). Completeness can be calculated with the following formula:

$$\%C = \left[1 + \left(\frac{Y - X}{X}\right)\right] x100$$

Where: %C = Percent completeness
Y = The number of valid data points
X = The total possible number of data points.

14.4 Field Quality Control

Field QC samples are used to assess the influence of sampling procedures and equipment used in sampling. They are also used to characterize matrix heterogeneity. For basic water quality analyses, quality control samples to be prepared in the field will consist of field blanks, field duplicates and matrix spikes. The number quality control samples are set to achieve an overall rate of at least 12% of all analyses for a particular parameter. The external QA samples are rotated among sites and events to achieve the overall rate of 4% each of field duplicate samples, field blanks, and matrix spikes. The frequency and acceptance limits of field quality control samples for this project are listed in Table 11.

Field Blanks

The purpose of analyzing field blanks is to demonstrate that sampling procedures do not result in contamination of the environmental samples. Field blanks will be prepared and analyzed for all analytes of interest at the rate of $\geq$ 3.33% of the total number of associated environmental samples. Field blanks will consist of laboratory-prepared blank water processed through the sampling equipment using the same procedures used for environmental samples. If any analytes of interest are detected at levels greater than the Reporting Limit (RL) for the parameter, the sampling crew should be notified so that the source of contamination can be identified (if possible) and corrective measures taken prior to the next sampling event. If the concentration in the associated samples is less than five times the value in the field blank, the results for the environmental samples may be unacceptably affected by contamination and should be qualified as below detection at the reported value.

Field Duplicates

The purpose of analyzing field duplicates is to demonstrate the precision of sampling and analytical processes. Field duplicates will be prepared at the rate of $\geq$ 3.33% of the total number of associated environmental

samples. Field duplicates will consist of two aliquots from the same composite sample, or of two grab samples collected in rapid succession. If an RPD greater than 25% is confirmed by reanalysis, environmental results will be qualified as estimated. The sampling crew should be notified so that the source of sampling variability can be identified (if possible) and corrective measures taken prior to the next sampling event.

14.5 Laboratory Quality Control

Laboratory QC is necessary to control the analytical process within method and project specifications, and to assess the accuracy and precision of analytical results. For basic water quality analyses, quality control samples prepared in the contract laboratory (s) will typically consist of equipment blanks, method blanks, laboratory control samples, laboratory duplicates and surrogate added to each sample (organic analysis).
The frequency and acceptance limits of laboratory quality control samples for this project are listed in Table 12.

Equipment Blanks
The purpose of analyzing equipment blanks (EB) is to demonstrate that sampling equipment is free from contamination. Prior to using sampling equipment for the collection of environmental samples, the laboratory responsible for cleaning and preparation of the equipment will prepare bottle blanks and sampler blanks. These will be prepared and analyzed at the rate of one each per piece of sampling equipment. The blanks will be analyzed using the same analytical methods specified for environmental samples. If any analytes of interest are detected at levels greater than the MDL, the source(s) of contamination should be identified and corrected, the affected equipment should be re-cleaned, and new equipment blanks should be prepared and analyzed. Sampler blanks will consist of laboratory-prepared blank water processed through the sampling equipment using the same procedures used for environmental samples.

Method Blanks
The purpose of analyzing method blanks is to demonstrate that the analytical procedures do not result in sample contamination. Method blanks (MB) will be prepared and analyzed by the contract laboratory at a rate of at least one for each analytical batch. Method blanks will consist of laboratory-prepared blank water processed along with the batch of environmental samples. If the result for a single MB is greater than the acceptance limits the source(s) of contamination should be corrected and the associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as below detection at the reported blank value.

Laboratory Control Samples
The purpose of analyzing laboratory control samples (LCS) is to demonstrate the accuracy of the analytical method. Laboratory control samples will be analyzed at the rate of one per sample batch. Laboratory control samples will consist of laboratory fortified method blanks. If recovery of any analyte is outside the acceptable range for accuracy, the analytical process is not being performed adequately for that analyte. In this case, if the matrix spikes are also outside the acceptable range, the LCS and associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as low or high biased.

Matrix Spikes and Matrix Spike Duplicates
The purpose of analyzing matrix spikes and matrix spike duplicates is to demonstrate the performance of the analytical method in a particular sample matrix. The number of matrix spikes is set to achieve an overall rate of at least 4% of all analyses for a particular parameter. Each matrix spike and matrix spike duplicate will consist of an aliquot of laboratory-fortified environmental sample. Spike concentrations should be added at five to ten times the reporting limit for the analyte of interest. If matrix spike recovery of any analyte is outside the acceptable range, the results for that analyte have failed the acceptance criteria. If recovery of laboratory control samples is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. Attempt to correct the problem (by dilution) and re-analyze the samples and the matrix spikes. If the matrix problem can't be corrected, qualify the results for that analyte as appropriate (low or high biased) due to matrix interference. If the matrix spike duplicate RPD for any analyte is greater

than the precision criterion, the results for that analyte have failed the acceptance criteria. If the RPD for laboratory duplicates is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. An attempt should be made to correct the problem (by dilution, concentration, etc.) and re-analyze the samples and the matrix spike duplicates. If the matrix problem can't be corrected, qualify the results for that analyte as not reproducible, due to matrix interference. Tables 11 and 12 present the QC requirements for water quality samples at specific criteria.

Table 11. (Element 14) Sampling (Field) QC.

Matrix: water
Sampling SOP: Appendix 3
Analytical Parameter(s): organophosphates, carbamates, herbicides, paraquat dichloride
Analytical Method/SOP Reference: Appendices 6-9
Sample locations: 15

Field QC	Frequency per sampling event/ Total number	Acceptance Limits
Equipment Blanks	One time per each piece of equipment for first event only	Less than Reporting Limit
Field Blanks	Approximately 4% / 11	Less than Reporting Limit
Cooler Temperature	Measured by analyzing lab at time of delivery	$\leq$ 4° C
Field Duplicate Pairs	Approximately 4% / 11	RPD $\leq$ 25%
Field Matrix Spikes	Approximately 4% / 11	70-125%

Table 12. (Element 14) Analytical QC.

Matrix: water
Sampling SOP: Appendix 3
Analytical Parameter(s): organophosphates, carbamates, herbicides, paraquat dichloride
Analytical Method/SOP Reference: Appendices 6-9
Sample locations: 15

Laboratory QC	Frequency/Number	Acceptance Limits
Method Blank	5%	<RL
Instrument Blank (CCB)	$\leq$12 hours	<RL
Lab. Duplicate	5%	$\leq$25% RPD
Lab. Matrix Spike	5%	70-125%
Lab. Control sample	5%	70-125%
Surrogates	1	70-125%

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Field measurement equipment will be checked for operation in accordance with the manufacturer's specifications. This includes battery checks, routine replacement of membranes, cleaning of conductivity electrodes on multi-parameter meters, performance of spin tests, and oiling and pivot adjustment on AA type current meters. Equipment will be inspected for damage when first handed out and when returned after use. Spare parts, including additional bolts, nuts, washers and other hardware for sampling equipment, are kept in AEAL sampling vehicles to be accessed during sampling if needed. Additional spare parts are kept at AEAL storage facilities and restocked as needed. AEAL maintains its equipment in accordance with its SOPs, which include procedures specified by the manufacturer and those specified by the method. See Table 13 for deficiency actions corresponding to sampling equipment. See SOP's in Appendices 4 & 5 for documentation of calibration.

Table 13. (Element 15) Testing, inspection, maintenance of sampling equipment and analytical instruments.

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
Oakton pH/CON 10 Multi-parameter meter	Rinsing of probe and electrode cleaning	AEAL sampling crews	One time per month If calibration fails calibrate and use backup meter	Appendix 5
USGS Price Type AA current meter	Spin test, clean and oil	AEAL sampling crews	Spin test before each use (min. 120 seconds) oil and adjust pivot if spin test fails	Appendix 4
Agilent /HP 6890GC-FPD	Injector cleaning Change septum; change insert; change columns	CDFG-WPCL Chemists	Injector: as needed Septum: weekly or at least once per month Insert: once every 2 months Columns: as needed	No SOP. Reference manufacturer literature
Agilent 1100 LC-MSD	Injector cleaning Change septum; change insert; change columns	CDFG-WPCL Chemists	Injector: as needed Septum: weekly or at least once per month Insert: once every 2 months Columns: as needed	No SOP. Reference manufacturer literature
Varian Saturn 4000 GC- MS/MS Ion trap	Injector cleaning Change septum; change insert; change columns	CDFG-WPCL Chemists	Injector: as needed Septum: weekly or at least once per month Insert: once every 2 months Columns: as needed	No SOP. Reference manufacturer literature

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

This section briefly describes analytical methods and calibration procedures used at the CDFG laboratory for samples that will be collected under this project.

Method calibration
Five to seven levels of standards are prepared to calibrate the analysis method. A linear regression is used including 0,0. The R squared value should be greater or equal to 0.995. Standards are run with the sample set to check for calibration integrity. Continuing calibration standard values should be within ±25% of calibration. If the residue amount falls outside calibration curve, the sample will be diluted and reanalyzed. A non-linear calibration may be necessary to achieve low detection limits or address specific instrumental techniques. Non-linear calibration is not to be used to compensate for detector saturation or to avoid instrument maintenance.

Table 14. (Element 16) Testing, inspection, maintenance of sampling equipment and analytical instruments.

Equipment / Instrument	SOP reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
Oakton pH/CON 10 Multi-parameter meter	Appendix 5	calibrated for pH and electrical conductivity against manufacturer standards	Prior to each sampling event	AEAL sampling crew
Agilent 6890 GC-FPD	No SOP. Reference manufacturer literature	5-7 point initial calibration	Beginning of each analytical run (every 10 samples)	CDFG-WPCL Chemist
Agilent 1100 LC-MSD	No SOP. Reference manufacturer literature	5 point initial calibration	Beginning of each analytical run; check every 10 samples	CDFG-WPCL Chemist
Varian Saturn 4000 GC- MS/MS Ion trap	No SOP. Reference manufacturer literature	5 point initial calibration	Beginning of each analytical run; check every 10 samples	CDFG-WPCL Chemist

17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Gloves, sample containers, and any other consumable equipment used for sampling will be inspected by the sampling crew on receipt and will be rejected and/or returned if any obvious signs of contamination (torn packages, etc.) are observed. Inspection protocols and acceptance criteria for laboratory analytical reagents and other consumables are documented in the CDFG Quality Assurance Manual. The laboratory QA Manual is available for review at the CDFG laboratory.

Table 15. (Element 17) Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies / Consumables	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Solvents	Use in extraction of reagent water	No target analytes above LOQ	1/batch	CDFG Chemist
Na_2SO_4	Use in extraction of reagent water	No target analytes above LOQ	1/batch	CDFG Chemist
NaCl	Use in extraction of reagent water	No target analytes above LOQ	1/batch	CDFG Chemist
Spiking solution	Analyze each batch with standards using GCMS	Not to exceed 10 x LOQ	1/batch	CDFG Chemist
Glassware	Visual examination	No chips, cracks or burn marks	As needed	CDFG Chemist

18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

The only non-direct measurements are from the AEAL's database of data from prior studies. The database is maintained in accordance with AEAL policy as stated earlier. The data will be reviewed against the data quality objectives stated in Element 7 and only that data meeting all of the criteria will be used in this project.

19. DATA MANAGEMENT

Data will be maintained as established in Element 9 above. Copies of field logs, copies of chain of custody forms, original preliminary and final lab reports, and electronic media reports will be sent to the Regional Board Project Manager. The field crew will retain original field logs. The CDFG laboratory will retain original chain of custody forms. The CDFG will retain copies of the preliminary and final data reports. Henry Calanchini will maintain the database and all project records in AEAL custody. AEAL project data is stored on a secure server with a four-partition memory so that if any single memory partition fails it can be rebuilt from the remaining three. Data from the server is backed up weekly.

The SWAMP database compatible field data sheets are returned to AEAL after each sampling event, copied and filed. AEAL project personnel enter field data, including field descriptions and water quality parameters, into the AEAL's SWAMP comparable TMDL database. Discharge measurement data from the field sheets are used to calculate discharges, which are then double-checked for accuracy by the AEAL QA Officer and entered into the database. Sample results from the CDFG laboratory are sent to the AEAL lab via electronic data deliverables (EDD). Results, as well as site codes, times and dates are uploaded by AEAL project personnel from the CDFG EDDs into the AEAL TMDL database with minor format changes. The production of data tables is generated from this database.

After data entry or data transfer procedures are completed for each sample event, data will be inspected by the AEAL QA Officer for data transcription errors, and corrected as appropriate.

In cases where environmental results are less than the reporting limit (RL) but greater than the method detection limit (MDL), the results will be flagged with a "DNQ" (Detected Not Quantified); e.g. an analytical result of 4 µg/L for an analyte with a reporting limit of 5 µg/L will be reported as: 4 µg/L DNQ, or: 0.004 ppb DNQ.

In cases where environmental results are less than the MDL (i.e. non-detects) the results will be reported as the MDL preceded by a negative (-) sign and flagged with an "ND" (Not Detected); e.g. an analytical result of "none detected" for an analyte with an MDL of 4 µg/L will be reported as: - 4 µg/L ND, or: - 0.004 ppb ND.

CDFG Data Management Protocol:
The laboratory staff person logging the sample(s) will carefully inspect each sample for chain-of-custody documentation FG 1000 (DFG Chain of Custody Record), sample labeling, packing lists, and for the condition of the custody seals, sample packing materials, sample containers and sample temperature. Any discrepancies or problems associated with sample shipment will be documented on the chain-of-custody form.

After inspection, the samples will be entered into the bound laboratory sample receiving logbook, and will be assigned a unique sample identification number. The following information shall be included on the COC when samples are logged-in:

Laboratory number (assigned when samples are submitted)
Laboratory storage location (refer or freezer no.)
Spill Title (if applicable)
Suspects name (if applicable)
Index-PCA code (if applicable)
Sampler's name, address and phone number
Date received by the laboratory
Analysis requested
Sample identification/location
Sample type (matrix)
Number of containers and container type
Sample preservation and temperature
Required report completion date
Signatures of person submitting samples and person receiving samples for the laboratory
Date samples received by the laboratory
Problem description (if applicable)
Incident location (if applicable)
Special instructions (if applicable)

The person logging the samples in will ensure that the samples are either retained in secure storage or are given directly to an authorized analyst. A copy of the chain-of-custody form will be used to provide analysis requirements to the analyst(s). This form will accompany the sample containers and/or prepared extracts as each authorized employee performs a required task on the samples. All samples will be logged into the LIMS (Laboratory Information Management System) database.

After all analyses have been completed and disposal of the sample is authorized, a designated sample custodian will make proper disposition of the sample with appropriate documentation. Disposal method and approximate disposal date will be noted in the laboratory log-in records. The completed chain-of-custody form(s) will be retained as a permanent part of the project record.

Procedures for analytical reporting will be as follows:

Retain all appropriate computer printouts and strip chart recordings in a binder (be sure information includes sample number, date and time).

Have all information clearly recorded so that a written data report can be made and reviewed.

Individual data reports shall be given to the Laboratory Supervisor for review prior to the preparation of the final report.

All quality control/analytical data will be reviewed for correctness of the analytical, calibration, and data reduction procedures used, and initialed by the section leader or laboratory supervisor before the accompanying data may be reported. If after being reviewed, a set of data is determined to be out of control, the quality assurance coordinator shall be notified and an appropriate course of corrective action will be prescribed. The analyst shall enter the corrective measures taken in the lab notebook, which will then be signed by the supervisor or QA officer. No additional analytical data will be generated until the problem has been identified and corrected.

The final reports contain an outline of the scope of the project, sample identification, methodologies performed, a discussion of any unusual circumstances regarding the project, and tabulated analytical results. This report is reviewed and signed by the person who prepared the analyses, and by the technical reviewer or supervisor. A signed copy of the report and COC will be kept in the binder. All data will be entered into the CDFG Laboratory Information Management System (LIMS). The database is updated frequently showing that the sample has been completed.

Hard copies of all chromatograms, area percent reports, and internal standard reports are generated and archived for each sample analyzed. Additionally, all phases of the analysis are archived digitally to ensure that the data remains retrievable.

GROUP C: ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS & RESPONSE ACTIONS

Measurement data must be consistently assessed and documented to determine whether project quality assurance objectives (QAOs) have been met, quantitatively assess data quality and identify potential limitations on data use. Assessment and compliance with quality control procedures will be undertaken during the data collection phase of the project:

- The AEAL project supervisor will assess the performance of the sampling procedures. Corrective action shall be carried out by the field sampling crew and reported to the quality assurance officer.

- The laboratory is responsible for following the procedures and operating the analytical systems within the statistical control limits. These procedures include proper instrument maintenance, calibration of the instruments, and the laboratory QC sample analyses at the required frequency (i.e., method blanks, laboratory control samples, etc.). Associated QC sample results are reported with all sample results so the project staff can evaluate the analytical process performance.

All project data must be reviewed as part of the data assessment. Review is conducted on a preparation batch basis by assessing QC samples and all associated field sample results.

Project data review established for this project includes the following steps:

- Initial review of analytical and field data for complete and accurate documentation, chain of custody procedures, analytical holding times compliance, and required frequency of field and laboratory QC samples;
- Evaluation of analytical and field blank results to identify random and systematic contamination;
- Comparison of all spike and duplicate results with project objectives for precision and accuracy;
- Assigning data qualifiers flags to the data as necessary to reflect limitations identified by the process; and
- Calculating completeness by matrix and analyte.

AEAL is responsible for ensuring that data qualifier flags are assigned, as needed, based on the established QC criteria.

Corrective Actions

During the course of sample collection and analysis in this study, the laboratory supervisors and analysts, and contractor project supervisor and team members will make sure that all measurements and procedures are followed as specified in this QAPP, and measurements meet the prescribed and acceptance criteria. If a problem arises, prompt action to correct the immediate problem and identify its root causes is imperative. Any related systematic problems must also be identified.

Problems about analytical data quality that require corrective action are documented in the laboratories' QA/QC Guidance. Problems about field data quality that may require corrective action are documented in the field data sheets.

Site Management

The AEAL project supervisor will observe field activities to ensure tasks are conducted according to the project specifications. The project supervisor is equipped with a cellular telephone for improved communication among the team members. Decontamination of field equipment will occur at a designated area assigned by the field manager. Access for sites is coordinated through the responsible agencies. This includes obtaining any necessary permits and coordinating with facilities and units where site activities will take place.

21. REPORTS TO MANAGEMENT

Data summary and final reports will be issued by AEAL according to the following table.

Table 16. (Element 21) QA Management Reports.

Type of Report	Frequency	Projected Delivery Dates(s)	Person(s) Responsible for Report Preparation	Report Recipients
Summarize winter storm sampling data (MS Access database)	one time only	4/22/2006	Henry Calanchini	CVRWQCB Project Manager
Statistical Analysis of lab QC's from winter sampling	one time only	4/22/2006	Dave Crane	AEAL Project Manager, CVRWQCB Project Manager
Draft report of winter sampling	one time only	5/1/2006	Henry Calanchini	CVRWQCB Project Manager
Final report of winter sampling	one time only	6/15/2006	Henry Calanchini	CVRWQCB Project Manager
Summarize all irrigation sampling data (MS Access database)	one time only	9/1/2006	Henry Calanchini	CVRWQCB Project Manager
Draft report of all irrigation sampling	one time only	10/1/2006	Henry Calanchini	CVRWQCB Project Manager
Final report of all irrigation sampling	one time only	11/15/2006	Henry Calanchini	CVRWQCB Project Manager
Statistical Analysis of lab QC's from irrigation sampling	one time only	9/1/2006	Dave Crane	AEAL Project Manager, CVRWQCB Project Manager

Final Technical Report

AEAL, will prepare a report after conducting data validation. The elements described below will be addressed and included in the report:

- Description of the project including the number of samples, analyses, completeness and any significant problems or occurrences that influence data use.
- The QA/QC activities performed during this project.
- QC sample results, type and number of samples including the results that did not meet the project objectives, and the impact on usability.
- Tables of analytical results for usable and unusable data.

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

Data generated by project activities will be reviewed against the data quality objectives cited in Element 7 and the quality assurance/quality control practices cited in Elements 14, 15, 16, and 17. Data will be separated into three categories: data meeting all data quality objectives, data failing to meet precision or recovery criteria, and data failing to meet accuracy criteria. Data meeting all data quality objectives, but with failures of quality assurance/quality control practices will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Data falling in the first category is considered usable by the project. Data falling in the last category is considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged with an appropriate SWAMP comparable data qualifier code.

In cases where field blank results exceed the acceptance criteria, data collected during the associated sample run will be qualified and reported as follows:

- Measured environmental sample concentrations greater than or equal to 5 times the field blank level will be reported with no qualification.
- Measured environmental sample concentrations less than 5 times the field blank level will be qualified as "less than" the measured value, e.g. if a field blank is equal to 1.5 µg/L, a measured environmental concentration of 4.0 µg/L will be reported as <4.0 µg/L.
- Any data qualifications resulting from QC analyses will be reported with the environmental data as appropriate.

23. VERIFICATION AND VALIDATION METHODS

Laboratory Data Review, Verification and Reporting

The CDFG QA Officer, Loc Nguyen, will use this QAPP for validating the data generated by the laboratory. The laboratory personnel will verify that the measurement process was "in control" (i.e., all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch. In addition, the CDFG laboratory will establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data.

The laboratory analyst performing the analyses is responsible for the reduction of the raw data generated at the laboratory bench to calculate the concentrations.

The analytical process includes verification or a quality assurance review of the data. This includes:

- Verifying the calibration samples for compliance with the laboratory and project criteria;
- Verifying that the batch QC were analyzed at a proper frequency and the results were within specifications;
- Comparing the raw data (e.g. chromatogram) with reported concentration for accuracy and consistency;
- Verifying that the holding times were met and that the reporting units and quantitation limits are correct;

- Determining whether corrective action was performed and control was re-established and documented prior to reanalysis of QC or project samples;
- Verifying that all project and QC sample results were properly reported and flagged; and
- Preparing batch narratives that adequately identify and discuss any problems encountered.

Specific Quality Control procedures are documented in the laboratory quality assurance manual. After the data have been reviewed and verified, the laboratory reports are signed for release and distributions. Raw data and supporting documentation is stored in confidential files by laboratory document control.

Only data, which have met data quality objectives, or data, which have acceptable deviations explained will be submitted by the laboratory. When QA requirements have not been met, the samples will be reanalyzed when possible and only the results of the reanalysis will be submitted, provided they are acceptable.

Data Validation

The AEAL QA Officer, Melissa Turner, will conduct data validation (data quality audit) to verify whether an analytical method has been performed according to the method and project specifications, and the results have been correctly calculated and reported. The AEAL will conduct the data validation prior to submitting the data to CVRWQCB. Specific items that are reviewed during data validation are:

- Chain of custody records
- Documentation of the laboratory procedures (e.g., standard preparation records, run logs, data reduction and verification)
- Accuracy of data reduction, transcription, and reporting
- Adherence to method-specific calibration procedures and quality control parameters
- Precision and accuracy of recorded results

24. RECONCILIATION WITH USER REQUIREMENTS

The pesticide concentration data generated in this project will be used by the Regional Board and others for the assessment of progress in reducing pesticide runoff into surface waters and for the comparison of current concentrations with criteria for the protection of freshwater ecosystems, such as the CDFG criteria listed in Element 5.3.

The diazinon concentration data in the Sacramento River in conjunction with data collected by the Sacramento Valley Water Quality Coalition on diazinon concentrations in the Feather River and the diazinon loads entering the Sacramento River from five tributary subwatersheds, will be compared to those allowable under the Sacramento and Feather River TMDL (Karkoski et al., 2003).

Concentration data from all other analytes will be used to quantify ambient levels of pesticides in the Sacramento, San Joaquin and Delta watersheds and in the development of TMDLs for tributaries within the Sacramento basin and Delta. All data will also be used within the context of the SWAMP database to further characterize pesticide concentrations within surface waters of the Central Valley.

Pesticide concentration data generated in this study will be of a known and documented quality so that regulatory decision makers and other stakeholders will know the relative accuracy of the measurements being used to support comparisons with monitoring data from previous studies, develop criteria for the protection of freshwater ecosystems, and determine compliance with regulatory requirements. Unless it is otherwise qualified, the pesticide data generated in this project will meet the Quality Assurance Objectives listed in Element 14. The reporting limits for diazinon and chlorpyrifos are below recommended criteria for the protection of aquatic ecosystems listed in Element 5.3, so the measurements will be sensitive enough to detect exceedances of these criteria. The final data report will indicate the level of completeness of the data generated

and indicate any times in which data meeting the Quality Assurance Objectives was not obtained. This information can be used in conjunction with concentration graphs, mass balances, and other tools to determine how well the data obtained represents the concentrations and loads of diazinon and chlorpyrifos, and the concentrations of other pesticides, that are present at the sites sampled during storm and irrigation runoff events.

25. LITERATURE CITED

Karkoski, J., Menconi, M., McClure, D., Davis, G. and Dyke, J., 2003. Amendments to the Water Quality Control Plan for the Sacramento and San Joaquin River Basins for the Control of Orchard Pesticide Runoff and Diazinon Runoff into the Sacramento and Feather Rivers. California Regional Water Quality Control Board – Central Valley Region. Sacramento, CA.

Lu, Z., G. Davis and J. Karkoski. 2005. Relative Risk Assessment for Pesticides Used in the Sacramento River Watershed. Draft report. Regional Water Quality Control Board, Central Valley Region.

Nichol, G., Reyes, E., and Ray, W., 2004. Electronic Template for SWAMP- Compatible Quality Assurance Project Plans- Version 1.0. California State Water Resources Control Board. Sacramento, CA.

Siepmann, S. and B. Finlayson. 2000. Water quality criteria for diazinon and chlorpyrifos: California Department of Fish and Game Administrative Report 00-3. pp59.

USEPA 2004(a). Code of Federal Regulations, Title 40, Volume 21, Chapter 1, Part 136. 40CFR136: Guidelines Establishing Test Procedures For the Analysis of Pollutants. July 1, 2004. US Government Printing Office Washington, DC, USA.

USEPA 1986. SW846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. US Government Printing Office, Superintendent of Documents, Washington, DC, USA.

26. REVISION LOG:

Date	Revision #	Reason for Revision	Approved By	Date

Appendix 1. 2005-06 Sacramento, San Joaquin, and Delta TMDL Monitoring Plan

Aquatic Ecosystems Analysis Laboratory
John Muir Institute of the Environment
1 Shields Avenue
Davis, California 95616

Monitoring Plan for Diazinon and Chlorpyrifos TMDL Compliance and Characterization of Usage for Selected other Pesticides in the Sacramento and San Joaquin River Basins and the Sacramento-San Joaquin Delta 2006

Henry Calanchini
January 2006

I. INTRODUCTION

In accordance with Clean Water Act Section 303(d), all states must identify "impaired" bodies of water and establish Total Maximum Daily Loads (TMDLs) for stressors that are the cause of the impairment. States must also develop monitoring and control plans for each stressor. In California, the State Water Resources Control Board and its nine subunits, the Regional Water Quality Control Boards (RWQCBs), are responsible for meeting section 303(d) requirements.

Numerous toxicity studies have found concentrations of the organophosphate pesticides (OPs) diazinon and chlorpyrifos in Sacramento and San Joaquin waterways at levels that result in significant mortality or reproductive toxicity to the zooplankton species *Ceriodaphnia dubia* (Werner et al. 2000, Kuivila & Foe 1995). Since that time several studies have been undertaken to further study the temporal and spatial occurrence of diazinon in the Sacramento River watershed and the Sacramento-San Joaquin Delta for the purposes of supporting TMDL development and observing any long-term changes in diazinon concentrations and loads in the Sacramento River watershed.

In 2003, the Central Valley Regional Water Quality Control Board (CVRWQCB) approved Water Quality Objectives and a TMDL for diazinon in the Sacramento and Feather Rivers. The Water Quality Objectives set maximum allowable diazinon concentrations in the Sacramento and Feather Rivers, and the TMDL sets maximum allowable diazinon loads that can be discharged to the Sacramento River from five "subwatersheds": the Sacramento River Above Colusa, the Butte/Sutter Basin, the Colusa Basin, the Feather River and the Natomas Basin/American River.

Since January 2003 the Aquatic Ecosystems Analysis Laboratory (AEAL) has performed the Water Quality Objective and TMDL compliance monitoring for the CVRWQCB in the Sacramento basin and the Delta. In 2006 the majority of the TMDL compliance monitoring will be performed by the Sacramento Valley Water Quality Coalition and the San Joaquin County and Delta Water Quality Coalition. The AEAL will continue to monitor two sites for TMDL compliance: The Sacramento River at Alamar and the Sacramento River at Freeport.

In addition to the TMDL compliance monitoring, the AEAL will perform: winter storm monitoring at five sites in the northern San Joaquin basin; winter storm and spring-summer irrigation runoff monitoring at four tributary sites in the Sacramento basin; and winter storm and spring-summer irrigation runoff monitoring four sites in the eastern Sacramento-San Joaquin Delta tributary area (Delta). The purpose of this non-compliance monitoring is to identify and characterize the increasing usage of other pesticides that have been identified as "high risk" to surface waters as determined by their chemical properties and usage (Lu 2005).

This document describes the sampling plan to investigate the concentrations of diazinon in the Sacramento River watershed associated with runoff events in January and February 2006 and to identify and characterize the presence of additional high risk pesticides in the surface waters of the Sacramento Valley, northern San Joaquin Valley and the Delta during winter storm events, and spring and summer irrigation events.

II. OBJECTIVES

The primary objectives of this sampling project are (1) to characterize the concentrations of diazinon being discharged to the Sacramento River during the 2005-2006 orchard dormant spray season and (2) to identify and characterize the presence of additional high risk pesticides in the surface waters of the Sacramento Valley and the Delta during winter storm events, and spring and summer irrigation events. The objective will be achieved via the following tasks:

- Sampling two sites on the Sacramento River – The Sacramento River at Alamar and Freeport for diazinon and other OP pesticides during one storm event in the 2005-2006 orchard dormant spray season.
- Using the concentrations found in the water collected for this study, and all available discharge estimates, calculate the loadings for diazinon at the Alamar and Freeport sites.
- Sampling five sites in the northern San Joaquin basin for selected organophosphates, carbamates, and herbicides during two winter storm events.
- Sampling four streams within the Sacramento basin for selected organophosphates, carbamates, and herbicides during the orchard dormant spray season and the spring and summer irrigation seasons.
- Sampling four streams within the Delta for selected organophosphates, carbamates, and herbicides during the orchard dormant spray season, and the spring and summer irrigation seasons.
- Sampling five streams within the Sacramento basin for the herbicide, propanil, during the rice-growing season.

III. PERSONNEL

Sample collection will be performed by the Aquatic Ecosystems Analysis Laboratory (AEAL) of University of California, Davis under Contract No. 02-210-150 with the Central Valley Regional Water Quality Control Board. The California Department of

Fish and Game (CDFG) will perform the sample analysis in their Fish and Wildlife Water Pollution Control Laboratory in Rancho Cordova, CA. The primary project personnel include a contract manager and a technical reviewer from the CVRWQCB, and a project manager and project supervisor from UC Davis.

Jay Rowan (CVRWQCB) - Contract Manager: The contract manager is responsible for obtaining all services and analytical results/reports from the CDFG Analysis Lab contractor.

Dr. Michael Johnson (UCD) - Project manager: The project manager will work with all assigned Regional Board monitoring staff directly to provide guidance on sampling locations and timing of sample collection. The project manager will inform monitoring staff about sample collection and sample transport to the analytical laboratory. The project manager will obtain a copy of the Chain of Custody (COC) after each sampling day from each sampling crew. The project manager will receive the chemical analysis results from CDFG lab contract manager and prepare a monitoring program report including lab analysis results.

Petra Lee (CVRWQCB) - Technical Reviewer: Technical Reviewer provides advice in determining the sampling sites, frequency, and time periods and the Technical Reviewer is responsible for overseeing budgetary expenses related to this monitoring study.

Henry Calanchini (AEAL) – Project Supervisor: The project supervisor will assist the project manager by hiring, training, and supervising all monitoring staff and contributing to the monitoring program report. The project supervisor will be responsible for monitoring spray application and weather conditions and in coordination with the technical reviewer, will determine when to begin sampling each storm event.

Field Technicians: Aaron King, Meghan Gilbart, Jon Katz, Joseph Kiernan, and Melissa Turner

IV. MONITORING PLAN

The monitoring sites for this study will located at Alamar and Freeport for the Sacramento River TMDL winter storm monitoring; the San Joaquin River at Patterson, the San Joaquin River at Lander Avenue, the Merced River at River Road, Del Puerto Creek at Vineyard Road, and Orestimba Creek at Kilburn Road for the high-risk pesticide winter storm monitoring in the northern San Joaquin basin; Gilsizer Slough, Live Oak Slough, Morrison Slough, and Angel Canal/Comanche Creek for the high-risk pesticide winter storm monitoring and the spring and summer irrigation monitoring in the Sacramento Valley; Pixley Slough, Mormon Slough, Little John Creek, and Lone Tree Creek for the high-risk pesticide winter storm monitoring

and the spring and summer irrigation monitoring in the Delta; Little Dry Creek, Butte Creek, Stone Corral Creek, Freshwater Creek, and Colusa Basin Drain for the spring propanil sampling. See Table 1 and Figures 1a, 1b, 2 and 3 for a list of the sites and their specific locations.

The Sacramento River at Freeport and at Alamar will be sampled once per day for eight consecutive days during one winter storm event. "High risk" pesticide monitoring sites in the Sacramento basin, northern San Joaquin basin, and Delta will be sampled once per day for two consecutive days for two storm events (n=4) during the winter storm-monitoring season. With the exception of the northern San Joaquin basin sites, the same sites will be sampled once every two weeks for eight consecutive weeks (n=4) during the spring (March-April) irrigation-monitoring season and once per week for four consecutive weeks during the summer (July) irrigation-monitoring season. The propanil sampling sites in the Sacramento basin will be sampled once per week for eight consecutive weeks from May-June. See Appendix 2 for monitoring schedules.

The Project Supervisor will be responsible for monitoring of pesticide application. Pesticide application information will be obtained by calling county agricultural commissioners offices. Storm events will only be sampled once it has been determined that widespread pesticide application has occurred. The Project Supervisor is also responsible for monitoring weather conditions and tracking storm fronts throughout the watershed. The determination of whether a particular storm constitutes a "storm event" will be aided by accessing data from various sources including precipitation data from the California Data Exchange Center (CDEC) http://cdec.water.ca.gov/ operated by the California Department of Water Resources (DWR), quantitative precipitation forecasts from the California Nevada River Forecast Center http://www.wrh.noaa.gov/cnrfc/qpf.php operated by the National Oceanic and Atmospheric Administration, and information from local and national weather sources.

The flexible trigger for determining the beginning of storm sampling is 0.5" of rainfall over the sampling area within a 24-hour period. Storm intensity, measured rainfall, predicted rainfall, level of soil saturation, and observed runoff are all factors to be considered when determining if a storm constitutes a "storm event" to be sampled. Once the determination to begin sampling has been made, sampling crews will be mobilized and sampling will commence either that day or on the following morning if there are not enough daylight hours left to safely complete the sampling route on the day of determination.

Samples at the Freeport Bridge will be collected from the walkway of the bridge using a 3-L Teflon bottle strapped to a weighted metal cage. The samples at the Merced River site we will be collected by lowering the 3-L Teflon bottle from the old highway bridge at the equally spaced intervals. The 3-L bottle will be lowered from

the water surface to the streambed and back at a uniform rate consistent with filling the bottle ¼ full at each vertical. After collecting the third vertical the Teflon bottle will be capped and the water agitated to ensure thorough mixing before the water is poured into a 1-L amber glass sample bottle. Samples at all other sites will be collected by strapping a 1-L amber glass sample bottle into a PVC pole sampler and dipping the bottle as close to the center of the channel as possible until the bottle is full. During high flows if a bridge is present the sample may be collected using the 3-L Teflon bottle as described above for safety purposes.

Each sample will be marked on the field sheet as either a "grab" sample if it is collected with a single dip of the pole sampler or from a single vertical using the 3-L Teflon bottle, or as an "integrated grab" sample if it is collected with the 3-L teflon bottle from two or more verticals across the stream channel width and mixed together to form a composite sample. If, at any site, the sampler does not believe the stream water to be well mixed, the 3-L teflon bottle will be used to collect a composite sample by partially filling the bottle at each of three or more verticals, agitating the composite sample and pouring the water into a 1-L amber glass sample bottle. The number of verticals will be recorded on the field sheet.

All samples will be placed in a cooler on wet ice and stored at 4°C until delivered to the analytical lab. If samples cannot be delivered on the day of collection they will be delivered the following morning. A chain of Custody (COC) form listing each sample will be completed. The analyzing laboratory will retain custody of the original COC and provide a copy to the AEAL for their records. The AEAL will provide copies of all COCs to the CVRWQCB.

At each site the following data will be measured (or observed) and recorded: *in-situ* measurements of water quality parameters (pH, temperature, specific conductance), weather conditions, stream conditions, approximate location in the stream at which the sample was collected and any pertinent observations (inputs, dead fish, etc). For specific procedures refer to Appendix 3: Standard Operating Procedures for Collecting Surface Water Samples in the Sacramento and San Joaquin River Basins and the Sacramento-San Joaquin Delta.

Table 1. 2005-06 Sacramento Basin and Delta TMDL and High Risk Pesticide Monitoring Sites.

Site ID	*Site Name*	*Latitude*	*Longitude*
Sacramento River TMDL Winter Storm Monitoring			
519LSAC52	Sacramento River at Freeport	38.45573	-121.50106
519LSAC55	Sacramento River at Alamar	38.67328	-121.62444
High Risk Pesticide Monitoring (winter storm and irrigation seasons) in the Sacramento Basin			
520LSAC23	Gilsizer Slough at South Township Road	39.01602	-121.68873
520LSAC24	Live Oak Slough at Nuestro Road	39.18533	-121.66148
520LSAC25	Morrison Slough at Luckehe Road	39.30494	-121.68909
520LSAC26	Angel Canal/Commanchee Creek at Crouch Avenue	39.68604	-121.88068
High Risk Pesticide Monitoring (winter storm and irrigation seasons) in the Delta			
531DEL501	Pixley Slough at Ham Lane	38.07474	-121.28630
531DEL502	Mormon Slough at Copperopolis Road	37.97166	-121.11253
531DEL503	Littlejohn Creek at Jack Tone Road	37.88962	-121.14605
531SJC503	Lone Tree Creek at Austin Road	37.85566	-121.18406
Sacramento Basin Rice Propanil Sampling			
520LSAC27	Little Dry Creek at Afton Road	39.42056	-121.85266
520LSAC28	Butte Creek at Afton Road	39.41988	-121.88002
520LSAC29	Stone Corral Creek at Four Mile Road/Excelsior Road	39.29363	-122.11562
520LSAC30	Freshwater Creek at Old Hwy 99 West	39.17725	-122.16121
520LSAC31	Colusa Basin Drain #1	38.81250	-121.77310
San Joaquin Basin TMDL Winter Storm Monitoring			
535MER546	Merced River at River Road	37.35044	-120.96097
541STC507	San Joaquin River at Patterson	37.49407	-121.07885
541MER522	San Joaquin River at Lander Avenue	37.29548	-120.85024
541STC516	Del Puerto Creek at Vineyard Road	37.52155	-121.14773
541STC518	Orestimba Creek at Kilburn Road	37.39935	-121.03194

Figure 1a. Four TMDL monitoring sites in the Sacramento River Basin to be monitored for pesticides during the 2006 orchard dormant spray and spring-summer irrigation seasons.

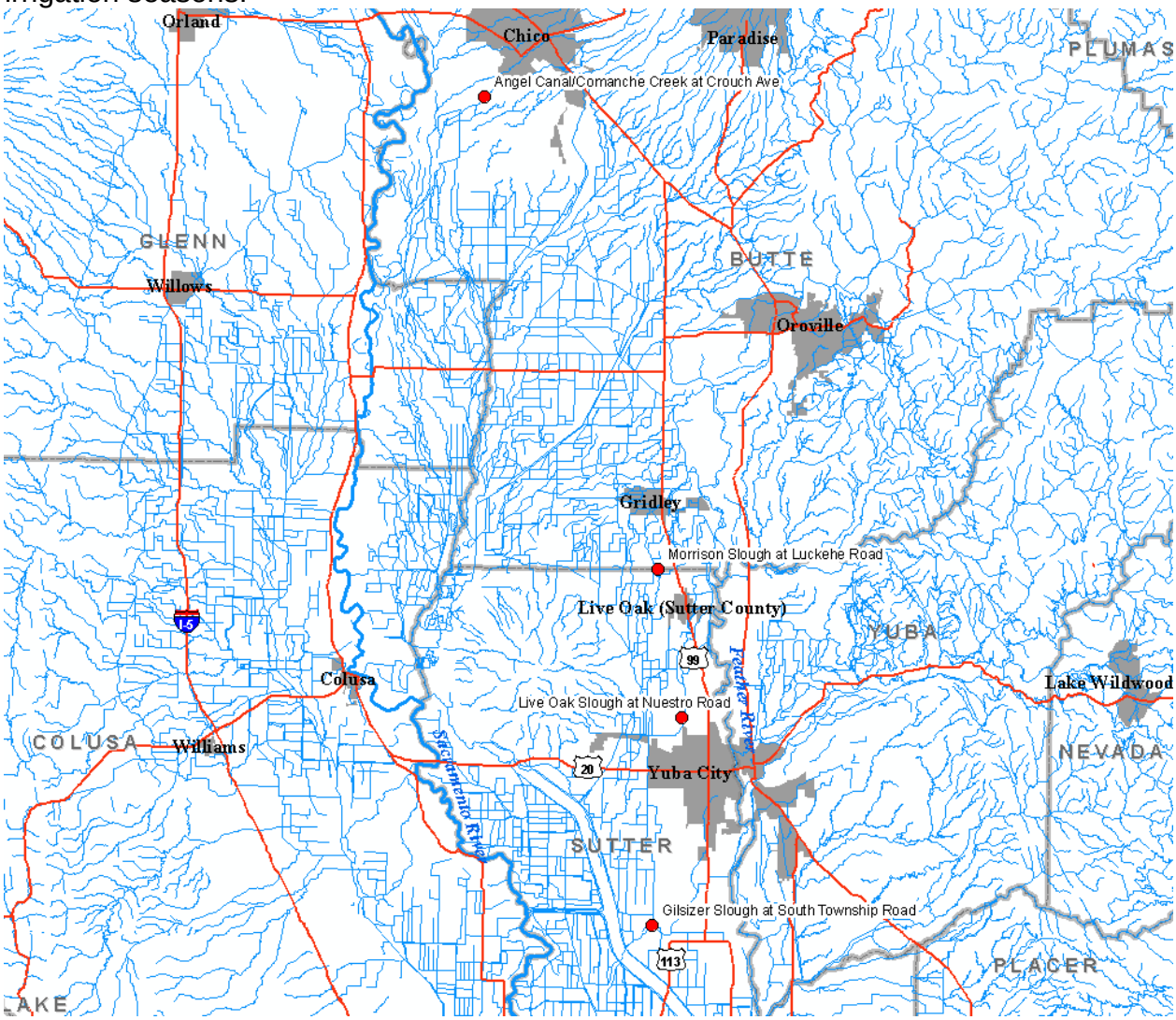


Figure 1b. Six TMDL monitoring sites in the Sacramento River Basin and Delta to be monitored for pesticides during the 2006 orchard dormant spray and spring-summer irrigation seasons.

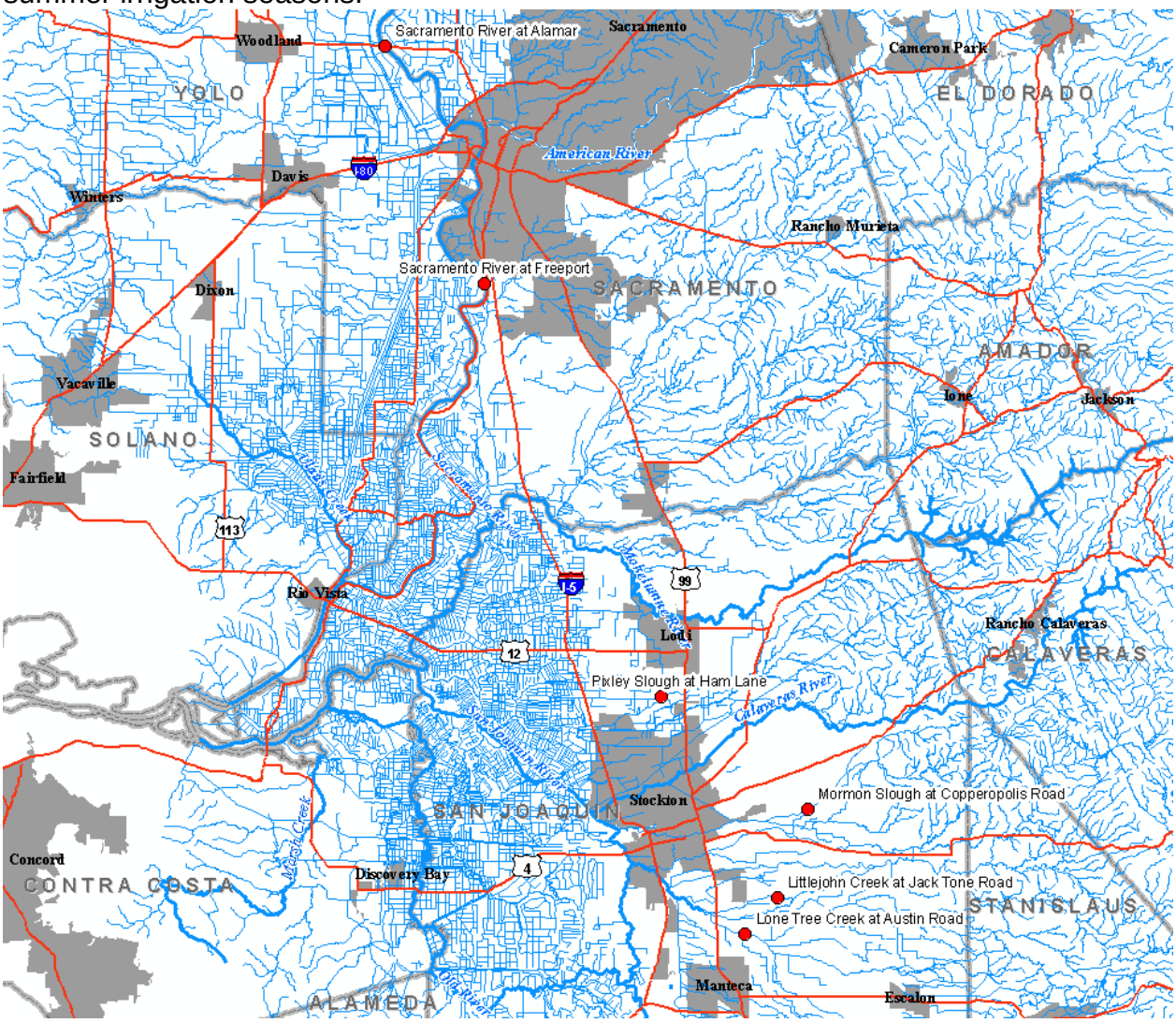


Figure 2. Five TMDL monitoring sites in the Sacramento River Basin to be monitored for propanil during the 2006 rice irrigation season.

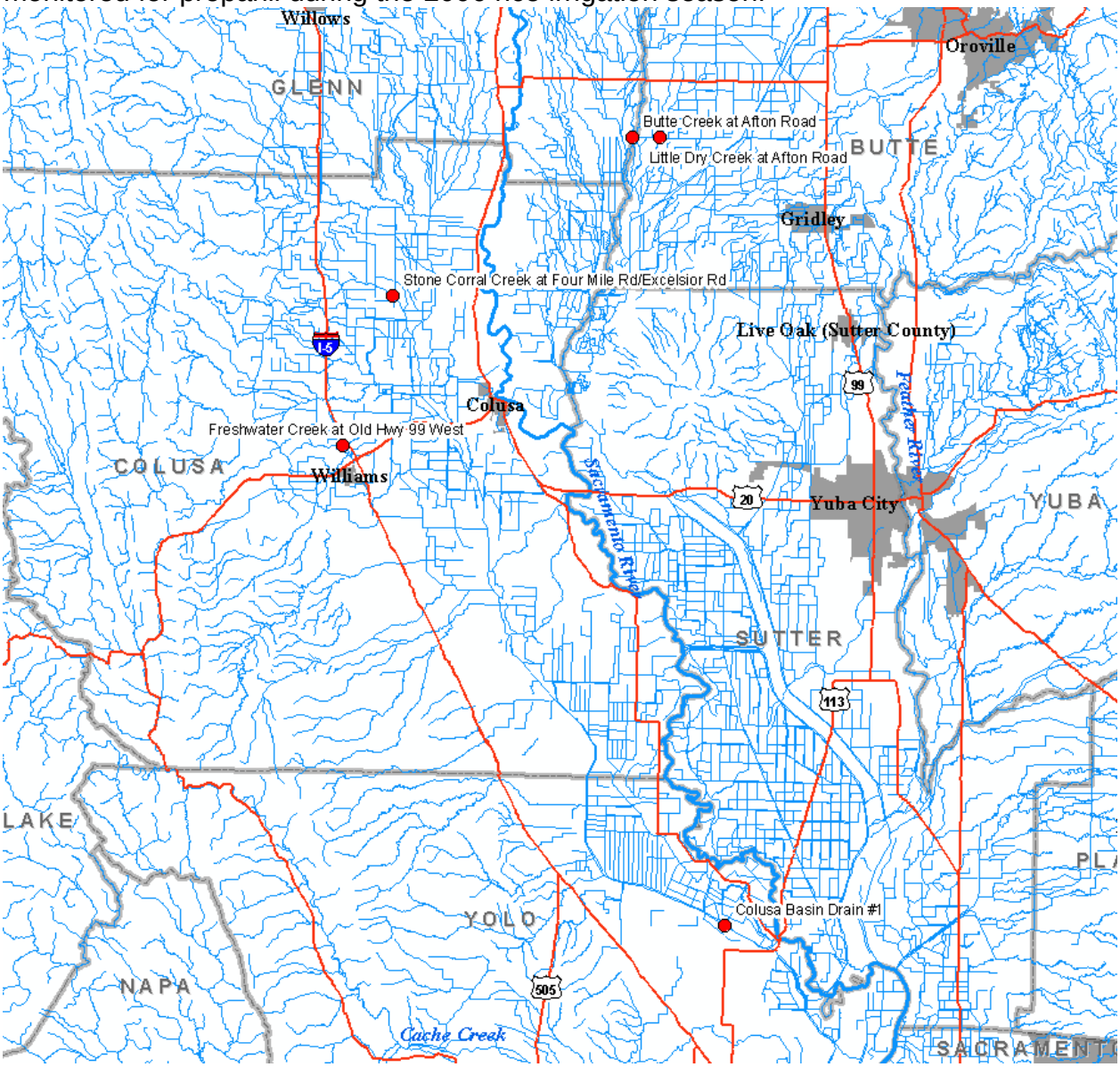
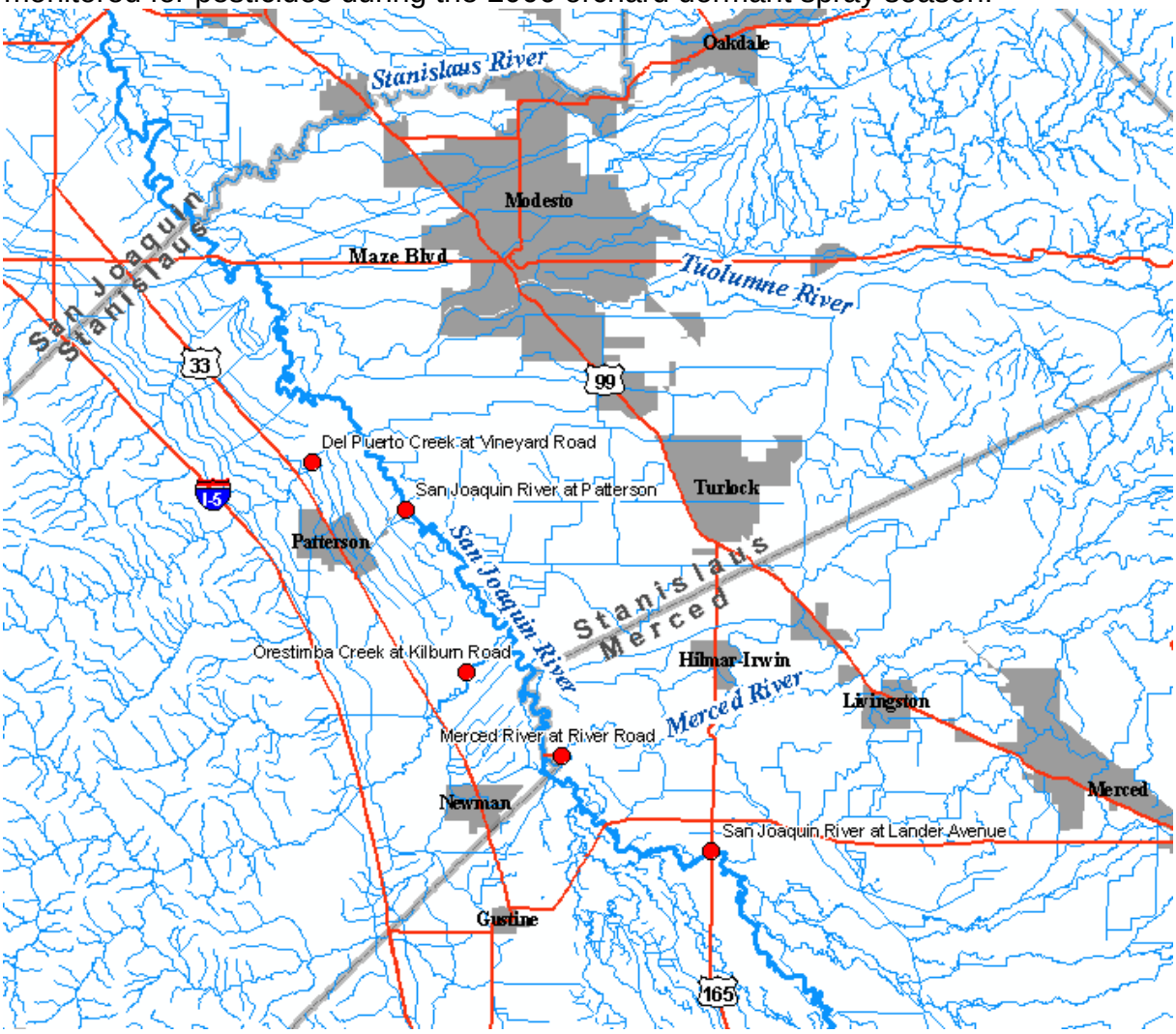


Figure 3. Five TMDL monitoring sites in the northern San Joaquin River Basin to be monitored for pesticides during the 2006 orchard dormant spray season.



V. CHEMICAL ANALYSIS

Chemical analyses will be performed by the California Department of Fish and Game's Fish and Wildlife Water Pollution Control Laboratory. Water samples will be analyzed for organophosphates, carbamates, and herbicides using the GC-FPD, LC-MSD, and GC-MSMS methods (see QAPP Appendices 6-9) Table 2 presents the pesticides to be analyzed, the chemical analytical methods, and reporting limits.

Table 2. List of pesticides and herbicides to be analyzed for in surface waters of the Sacramento basin and Sacramento-San Joaquin Delta.

Class/Method	Analyte	Method Detection Limit (ppb)	Reporting Limit (ppb)
Organophosphates	chlorpyrifos	0.003	0.005
GC-FPD	diazinon	0.003	0.005
	azinphos methyl	0.030	0.050
	malathion	0.030	0.050
	methidathion	0.030	0.050
	methyl parathion	0.010	0.050
LC-MSD	paraquat dichloride	0.200	0.500
Carbamates	diuron	0.002	0.005
LC-MSD	carbofuran	0.010	0.020
	carbaryl	0.010	0.020
	methiocarb	0.150	0.250
	aldicarb	0.010	0.050
	captan	0.050	0.100
	linuron	0.002	0.005
	methomyl	0.010	0.020
Herbicides	propanil	0.050	0.100
GC-MSMS	propargite	0.200	0.500
	oxyfluorfen	0.020	0.050
	trifluralin	0.050	0.100

VI. QUALITY ASSURANCE/QUALITY CONTROL

Quality control will be conducted in accordance with the methods outlined in Appendix 3: Standard Operating Procedure for Collecting Surface Water Samples in the Sacramento and San Joaquin River Basins and the Sacramento-San Joaquin Delta. Quality control samples will consist of field blanks (n=14), matrix spikes (n=14) and sequential duplicates (n=14). The total number of quality control samples (n= 33) is equal to 13.8% of the total number of primary samples (n=304). Quality control samples will be split evenly among the sites and sampling seasons. See Appendix A for schedules of quality control samples.

VII. DATA REPORT

Two (2) data reports will be made; one each for the storm season monitoring and the irrigation season monitoring. The final data reports will summarize the activities

conducted to generate the data including sample collection, storage, and analysis. The data report will contain, as an appendix, a CD containing, in tabular format, all data generated during this project, as well as the diazinon load estimates for all sites and sampling times for which concentration and flow data are available. The report will also include the results of the analysis of Quality Control samples and an assessment of the overall quality of the data generated in comparison to the goals described in the Quality Assurance Project Plan (QAPP). A preliminary draft of the storm season and TMDL compliance monitoring data report should be submitted to the CVRWQCB by May 1, 2006. A preliminary draft of the irrigation season data report should be submitted to the CVRWQCB by October 1, 2006. Following a review period of no longer than two (2) weeks, Regional Board staff will submit any comments they have on the preliminary drafts. The storm season and TMDL compliance monitoring report will be finalized by June 15, 2006 and the irrigation season monitoring report will be finalized by November 15, 2006.

VIII. TIME TABLE

Field Sampling: January 2006 through July 2006
Chemical Analysis: Results to be supplied within four weeks of sample delivery
Draft storm season report: to CVRWQCB by May 1, 2006; finalized by June 15, 2006.
Draft irrigation season report: to CVRWQCB by October 1, 2006; finalized by November 15, 2006.

IX. REFERENCES

Kuivila, K.M., and Foe, C.G., 1995. Concentrations, Transport and Biological Effects of Dormant Spray Pesticides in the San Francisco Estuary, California. Environmental Toxicology and Chemistry, 14:7, 1141-1150.

Lu, Z., G. Davis and J. Karkoski. 2005. Relative Risk Assessment for Pesticides Used in the Sacramento River Watershed. Draft report. Regional Water Quality Control Board, Central Valley Region.

Werner, I., Deanovic, L.A., et al., 2000. Insecticide-caused toxicity to Ceriodaphnia Dubia (Cladocera) in the Sacramento-San Joaquin River Delta, California, USA. Bulletin of Environmental Contamination and Toxicology, 19:1, 215-227.

Appendix 2. Schedule of Primary and Quality Control Samples

Analyses Key
A) Organophosphates by GC-FPD "Short List" (chlorpyrifos, diazinon, azinphos methyl, malathion, methidathion, methyl parathion)
B) Paraquat dichloride by LC-MS
C) Carbamates by LC-MS (diuron, carbofuran, carbaryl, methiocarb, aldicarb, captan, linuron, methomyl)
D) Herbicides by GC-MSMS (propanil, propargite, oxyfluorfen, trifluralin)

Primary and Quality Control (QC) Sample Schedule for Winter Storm Sampling in the Sacramento Basin								
	Gilsizer Slough at South Township Road 520LSAC23		**Live Oak Slough at Nuestro Road** 520LSAC24		**Morrison Slough at Luckehe Road** 520LSAC25		**Angel Canal/Comanche Creek at Crouch Avenue** 520LSAC26	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Storm 1/ Day 1	A, C, D	MS (A)	A, C, D		A, C, D		A, C, D	
Storm 1/ Day 2	A, C, D		A, C, D	EB (C)	A, C, D		A, C, D	
Storm 2/Day 1	A, C, D		A, C, D		A, C, D	DP (A)	A, C, D	
Storm 2/Day 2	A, C, D		A, C, D		A, C, D		A, C, D	MS (C)
MS: Matrix Spike		EB: Environmental Blank			DP: Duplicate			

	Sacramento River at Alamar 519LSAC55		**Sacramento River at Freeport** 519LSAC52	
	Primary	QC	Primary	QC
Day 1	A		A	
Day 2	A		A	
Day 3	A	MS	A	
Day 4	A		A	
Day 5	A		A	
Day 6	A		A	DP
Day 7	A		A	
Day 8	A		A	

Analyses Key
A) Organophosphates by GC-FPD "Short List" (chlorpyrifos, diazinon, azinphos methyl, malathion, methidathion, methyl parathion)
B) Paraquat dichloride by LC-MS
C) Carbamates by LC-MS (diuron, carbofuran, carbaryl, methiocarb, aldicarb, captan, linuron, methomyl)
D) Herbicides by GC-MSMS (propanil, propargite, oxyfluorfen, trifluralin)

Primary and Quality Control (QC) Sample Schedule for March-April Irrigation Sampling in the Sacramento Basin								
	Gilsizer Slough at South Township Road 520LSAC23		**Live Oak Slough at Nuestro Road** 520LSAC24		**Morrison Slough at Luckehe Road** 520LSAC25		**Angel Canal/Comanche Creek at Crouch Avenue** 520LSAC26	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Week 1	A, C	EB (A)	A, C		A, B		A, B	
Week 3	A, C		A, C	DP (C)	A, B		A, B	
Week 5	A, C		A, C		A, B	DP (A)	A, B	
Week 7	A, C		A, C		A, B		A, B	MS (B)
MS: Matrix Spike		EB: Environmental Blank		DP: Duplicate				

Primary and Quality Control (QC) Sample Schedule for July Irrigation Sampling in the Sacramento Basin								
	Gilsizer Slough at South Township Road 520LSAC23		**Live Oak Slough at Nuestro Road** 520LSAC24		**Morrison Slough at Luckehe Road** 520LSAC25		**Angel Canal/Comanche Creek at Crouch Avenue** 520LSAC26	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Week 1	D	EB (D)	D		D		D	
Week 2	D		D	DP (D)	D		D	
Week 3	D		D		D	EB (D)	D	
Week 4	D		D		D		D	MS (D)
MS: Matrix Spike		EB: Environmental Blank		DP: Duplicate				
D) Herbicides by GC-MSMS (propanil, propargite, oxyfluorfen, trifluralin)								

Analyses Key
A) Organophosphates by GC-FPD "Short List" (chlorpyrifos, diazinon, azinphos methyl, malathion, methidathion, methyl parathion)
B) Paraquat dichloride by LC-MS
C) Carbamates by LC-MS (diuron, carbofuran, carbaryl, methiocarb, aldicarb, captan, linuron, methomyl)
D) Herbicides by GC-MSMS (propanil, propargite, oxyfluorfen, trifluralin)

Primary and Quality Control (QC) Sample Schedule for Winter Storm Sampling in the Stockton Area								
	Pixley Slough at Ham Lane 531DEL501		**Mormon Slough at Copperopolis Road** 531DEL502		**Littlejohn Creek at Jack Tone Road** 531DEL503		**Lone Tree Creek at Austin Road** 531SJC503	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Storm 1/ Day 1	A, C	MS (A)	A, C, D		A, C, D		A, C, D	
Storm 1/ Day 2	A, C		A, C, D	EB (C)	A, C, D		A, C, D	
Storm 2/Day 1	A, C	DP (A)	A, C, D		A, C, D	DP (C)	A, C, D	
Storm 2/Day 2	A, C		A, C, D	EB (A)	A, C, D		A, C, D	MS (C)
MS: Matrix Spike		EB: Environmental Blank		DP: Duplicate				

Primary and Quality Control (QC) Sample Schedule for March-April Irrigation Sampling in the Stockton Area								
	Pixley Slough at Ham Lane 531DEL501		**Mormon Slough at Copperopolis Road** 531DEL502		**Littlejohn Creek at Jack Tone Road** 531DEL503		**Lone Tree Creek at Austin Road** 531SJC503	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Week 1	A, B	EB (A)	A, B		A, B		A, B, C	
Week 3	A, B		A, B	DP (B)	A, B		A, B, C	
Week 5	A, B		A, B		A, B	MS (A)	A, B, C	
Week 7	A, B		A, B		A, B		A, B, C	EB (B)
MS: Matrix Spike		EB: Environmental Blank		DP: Duplicate				

Analyses Key
A) Organophosphates by GC-FPD "Short List" (chlorpyrifos, diazinon, azinphos methyl, malathion, methidathion, methyl parathion)
B) Paraquat dichloride by LC-MS
C) Carbamates by LC-MS (diuron, carbofuran, carbaryl, methiocarb, aldicarb, captan, linuron, methomyl)
D) Herbicides by GC-MSMS (propanil, propargite, oxyfluorfen, trifluralin)

Primary and Quality Control (QC) Sample Schedule for July Irrigation Sampling in the Stockton Area								
	Pixley Slough at Ham Lane 531DEL501		**Mormon Slough at Copperopolis Road** 531DEL502		**Littlejohn Creek at Jack Tone Road** 531DEL503		**Lone Tree Creek at Austin Road** 531SJC503	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Week 1	D	EB (D)	D		D		D	
Week 2	D		D	MS (D)	D		D	
Week 3	D		D		D	EB (D)	D	
Week 4	D		D		D		D	DP (D)
MS: Matrix Spike		EB: Environmental Blank		DP: Duplicate				

Primary and Quality Control (QC) Sample Schedule for May-June Propanil Sampling in the Sacramento Basin										
	Little Dry Creek at Afton Road 520LSAC27		**Butte Creek at Afton Road** 520LSAC28		**Stone Corral Creek at Four Mile Road/Excelsior Road** 520LSAC29		**Freshwater Creek at Old Hwy 99 West** 520LSAC30		**Colusa Basin Drain #1** 520LSAC31	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Week 1	D	EB	D		D		D		D	
Week 2	D		D		D		D		D	
Week 3	D		D	MS	D		D		D	
Week 4	D		D		D	DP	D		D	
Week 5	D		D		D		D		D	
Week 6	D		D		D		D	MS	D	
Week 7	D		D		D		D		D	
Week 8	D		D		D		D		D	DP
MS: Matrix Spike			EB: Environmental Blank			DP: Duplicate				

Analyses Key
A) Organophosphates by GC-FPD "Short List" (chlorpyrifos, diazinon, azinphos methyl, malathion, methidathion, methyl parathion)
B) Paraquat dichloride by LC-MS
C) Carbamates by LC-MS (diuron, carbofuran, carbaryl, methiocarb, aldicarb, captan, linuron, methomyl)
D) Herbicides by GC-MSMS (propanil, propargite, oxyfluorfen, trifluralin)

Primary and Quality Control (QC) Sample Schedule for Winter Storm Sampling in the San Joaquin Basin

	Merced River at River Road 535MER546		**San Joaquin River at Patterson** 541STC507		**San Joaquin River at Lander Avenue** 541MER522		**Del Puerto Creek at Vineyard Road** 541STC516		**Orestimba Creek at Kilburn Road** 541STC518	
	Primary	QC	Primary	QC	Primary	QC	Primary	QC	Primary	QC
Storm 1/ Day 1	B, C, D	MS (B)	B, C, D	DP (D)			A, B, C, D		A, B, C, D	
Storm 1/ Day 2	B, C, D		B, C, D				A, B, C, D	EB (D)	A, B, C, D	MS (A)
Storm 2/Day 1	B, C, D	EB (B)			B, C, D	MS (C)	A, B, C, D	DP (C)	A, B, C, D	
Storm 2/Day 2	B, C, D				B, C, D	DP (B)	A, B, C, D		A, B, C, D	EB (A)
MS: Matrix Spike			EB: Environmental Blank			DP: Duplicate				

Appendix 3. Surface Water Sample Collection SOP

Standard Operating Procedure for Collecting Surface Water Samples in the Sacramento and San Joaquin River Basins and the Sacramento-San Joaquin Delta

1. Labeling the sample bottle

- Use pre-printed labels for each site. The label should include the site name, ID number, date, sample time, and your initials
- Complete the printed label with an extra-fine-point Sharpie. Cover the entire label with a piece of clear tape to prevent peeling
- Use 24-hour military time for the sample time; round to the nearest 10 minutes. For example: a sample collected at 09:52 would have the sample time on the label and Chain of Custody (COC) form rounded off to 09:50; a sample collected at 09:57 would be rounded up to 10:00; 09:55 would also be rounded up to 10:00. Use the following format for the date: mm/dd/yy

Sacramento River at Freeport
Date__01/10/06_____
Time_10:50__Initials_HJC__
I.D. 519LSAC52

2. Check the Quality Control Schedule to see if a QC sample is scheduled for the site

If so, label an additional 1L amber glass bottle according to the instructions in Step 5 below. Read the QC sampling procedure before sampling.

3. Fill out Field Sheet at each sampling site

How to fill out a field sheet:

Sampling Information

- Sampling Type is already filled out. Add sampler initials
- Sampler Bottle: 1L amber bottles are glass, 3L bottles are Teflon
- Sampling Method: vertical integrated grab is from a bridge, grab is from the bank

- Stage: will become apparent with experience, also can be researched later on the web or read from a staff gage if present

Sample Collected

- If a quality control sample is scheduled, place a check beside type of sample
- Sampling Time: Record rounded sample time

Field Measurements

Use Oakton pH/conductivity/temp meters; allow the probe to soak in native water for a few minutes for the reading to stabilize. Note the values for temperature, pH and EC on the field sheet along with the appropriate units (e.g. ^{o}C ,mS, µS,).

- BANK SAMPLE: measure directly from river edge
- BRIDGE SAMPLE: If you have an Oakton meter with a 100' probe, measure the parameters directly in the river at the center of the channel. If not, use the following procedure: after pouring off the sample use excess water from the 3L Teflon bottle for the field measurements; rinse the probe and plastic container with water from the 3L bottle before pouring another portion into the measuring container. Measure water parameters immediately after pouring off the sample so that conditions (temperature) do not change
- Flow and stage fields will be completed in the lab by getting information from CDEC or USGS web sites; please note source, date of receiving the information and your initials on the field sheet

At the end of the day fill the electrode storage cap with electrode storage solution before placing the meter in its case.

Recalibrate the Oakton pH/conductivity/temp meters once per month. Record recalibration date on a piece of labeling tap and affix to the inside panel of the meter case.

Note anything significant or unusual under Observations on the field sheet; for example waste disposal, irrigation runoff, foam on water surface, dead fish, etc.

Original field sheets stay with UC Davis in a prepared folder at the IOE.

4. How to collect a sample

Always wear clean gloves during sampling procedure!

BANK

a) Using bungee cord, affix 1L amber glass bottle to sampling pole
b) Check to insure the bottle is secure
c) Remove the cap (wear clean glove!)
d) Immerse the bottle until bubbles stop. Fill completely; do not leave any headspace
e) Replace the cap (still wearing the clean glove!)

f) Rinse the outside of the bottle with deionized water
g) Slip the bottle into a protective sleeve
h) Place sample directly into a cooler (up to 15 1L bottles can be placed in one cooler). Make sure there is no glass-to-glass contact

BRIDGE SAMPLE

1. Put on your orange safety vest. Always be aware of traffic and use caution while sampling from a bridge
2. At the van, put the 3L Teflon bottle into the TECHMA cage, secure it with the bungee cord (you will loose the bottle, if the bungee cord is not strapped around the bottle!), and remove the cap
3. Wearing leather gloves, carefully lower the bottle from the bridge railing to the water surface. Do not lower too fast or the bottle may be propelled from the cage upon impact. Perform a triple rinse with native water. Fill the bottle at least ¼ full for each rinse
4. To collect the sample, fill the bottle 1/4th at each of three equally spaced verticals (submerge for about 3-5 seconds), being careful to avoid contact between the bottle and anything but river water, especially when moving between verticals
5. Return to the van
6. Remove the 3L bottle from the TECHMA cage and swirl the water until completely mixed
7. The second person has already labeled the sample bottle. While wearing clean gloves the second person removes the bottle cap and holds the sample bottle as the sampler pours from the 3L Teflon bottle into the sample bottle. After the sample bottle is completely filled the second person then recaps the sample bottle
8. Rinse the outside of the sample bottle with deionized water, place the bottle in a protective sleeve and store it in the cooler.

The last thing to do before filling any amber glass sample bottle, regardless of method, is to remove the lid. The first thing to do after filling any amber glass sample bottle, regardless of method, is to replace the lid. If you have more than one sample bottle to fill, remove each lid just prior to filling the bottle

Clean the 3L bottle after sampling with the following procedure:

- While wearing gloves, add 10% liquinox soap mixture (2-3 squeezes) and approximately 50ml of deionized water to the Teflon bottle. Place the cap on the bottle and swirl the soap around inside the bottle until the entire inside surface has been covered with suds. Un-cap the bottle and pour the soap onto the ground. Rinse the bottle and cap using deionized water until no suds remain inside the bottle or on the cap
- Poor 5-10ml of methanol into the bottle and swirl, with the cap on, until methanol has covered the entire inside surface of the bottle. Carefully pour the waste methanol into the

methanol waste container. Seal the methanol bottle and waste container with Parafilm to prevent fume leakage. *Methanol is dangerous—do not inhale or touch!*

The 3L bottle is ready for the next sampling and should be stored, with the cap on, inside the TECHMA cage

5. If scheduled collect a quality control sample

View the QC Schedule to find out which type of QC sample you should collect that day

-- ***Field duplicate:***

a) Collect both samples simultaneously. If using a pole sampler place two bottles in the sampler. If using the TECHMA fill the 3L Teflon bottle with enough water for both the environmental and duplicate samples
b) Mark the sampling time of the duplicate sample by adding **3 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then duplicate time is 14:03). **Do not** indicate *duplicate* on the label or on the COC!

-- ***Matrix Spike:***

Collect **TWO** bottles of water; one for the matrix spike (MS) and one for the matrix spike duplicate (MSD). For both samples add **9 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then spike time is 14:09) and mark as "matrix spike" on the **COC** *and* **label**. It should be made obvious so that the lab knows that this sample needs to be spiked. The MSD will be labeled exactly the same as the MS.

BRIDGE SAMPLE

a) From the single 3L Teflon filled using the procedure above pour the collected water into two 1L bottles; one for the environmental sample and one for the matrix spike.

BANK SAMPLE

b) Fill two 1L bottles with one reach of the pole sampler; one for the environmental sample and one for the matrix spike.

-- ***Blank sample:***

Do not indicate blank on label or on COC. Time offset: add **1 minute** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then blank time is 14:01).

BRIDGE SAMPLE

BEFORE TAKING ENVIRONMENTAL SAMPLE:

a) Rinse the clean 3L Teflon bottle three times with deionized water (approximately 50ml for each rinse)

b) Fill the 3L bottle 2/3 full with deionized water and pour into a 1L bottle for the blank

BANK SAMPLE

Fill one 1L bottle with deionized water for the blank

Whoever did not fill out the field sheet and COC should double check all of the recorded times for completeness and error at the end of the sampling day

Check ice level

The temperature of the ice chest should be around 4°C. Make sure to add ice if necessary.

6. Deliver samples within 48 hours

Samples need to be dropped of at:

- **(1L amber glass bottles)**
  California Department of Fish and Game, Fish and Wildlife Water Pollution Control Laboratory, 2005 Nuimbus Road, Rancho Cordova, CA. Responsible Person: Abdou Mekebri, amekebri@ospr.dfg.ca.gov, *open from 8 am to 5 pm* after hours call Abdou Mekebri (916) 358-4396.
  No drop off on weekends or on holidays unless pre-arranged! (For storage in our facility or somewhere else over the weekend make sure that there is enough ice in the cooler and the temperature stays at 4 degrees C)

7. Complete Chain of Custody form

Complete a Chain of Custody form for each sampling day.

- The original COC's for the 1L amber glass bottles will stay in the CDFG Lab. Be sure to have Abdou Mekebri (or other recipient) make you a copy of the COC. Upon return to the IOE place our copy of the COC in the prepared folder at the IOE. After faxing, put your name, date, and time of fax on the copy and file it

Sample transfer between field staff and laboratory is documented by **signing and dating** "relinquished by" and "received by" blocks whenever sample possession changes. The document must have both yours **and** the lab's signature.

Appendix 4. Standard Operating Procedure for Price Type AA Current Meter

Standard Operating Procedure for Velocity Measurement and Discharge Calculation Using the Price Type AA Current Meter with a Wading Rod or a Bridge Board and Sounding Reel

(Revised June 2004 HJC)

Background

Stream discharge is the volume of water passing a cross-section per unit of time and is generally measured in cubic feet per second (cfs) or cubic meters per second (cms). The cross-sectional area is measured by stretching a tape across the stream to determine width, and recording depths using a wading rod or bridge board and sounding reel. For accuracy there should be a minimum of 20-30 verticals, or points, at which the velocity is measured in any particular stream, with no more than 10% of the total discharge in any rectangular subsection to ensure that a valid average discharge is measured. For measuring discharge, follow the steps below.

Procedures

WADING ROD METHOD

1. Select a cross section that best meets the following criteria:
   - Converging flow (i.e., cross-sectional area decreasing downstream) without areas of near-zero velocity or eddies.
   - Absence of backwater conditions
   - Smooth cross section with minimal flow obstructions upstream or downstream.
   - Depth shallow enough to provide safe wading conditions.

   Remove any large stones, sticks, vegetation and other objects immediately upstream and downstream of the measurement section.
2. Stretch a tape between the endpoints (width) of the channel making sure that the tape is perpendicular to the banks of the stream. To obtain an accurate discharge measure at least 20-30 verticals. The verticals should be spaced so that no subsection has more than 10% (ideally 5%) of the total discharge. Equal widths of partial sections across the entire cross section are not recommended unless the discharge is well distributed. Make the width of the partial sections less as depths and velocities becomes greater. If the stream is small (e.g. < 4ft wide) then an approximation can be used to set the amount of verticals. For example, 15 verticals for a 4ft wide stream should be sufficient. On the field sheet record the reading from your tape at the right (REW) and left (LEW) water's edge of the channel.
3. Remove the meter from the protective carrying case. Check the pivot before using the meter. The point should be sharp and the pivot should be straight. If the pivot is damaged in any way replace it with the spare pivot. Check to make sure that the pivot was lubricated after the previous use. Use only one drop of oil on the pivot. See **Appendix B** for care and transport of current meter.
4. Perform a spin test of the bucket wheel. Holding the meter upright, with the pivot in a vertical position, spin the bucket wheel with your finger. The bucket wheel should spin, without additional help, for a minimum of two minutes before coming to rest. If the bucket wheel stops before two minutes, replace the pivot and perform another spin test. Ideally the spin test should be performed inside a vehicle or other closed space to prevent wind influence.
5. To ensure an accurate reading, the meter must be completely submerged under water and free of interference. Make notes about boulders, snags, pier influences or other obstructions that may bias the

actual flow. Estimate the area influenced by these obstructions. Record on the discharge field sheet which bank you begin your measurements from by writing the abbreviations LEW (left edge water) or REW (right edge water) next to that vertical. Left and right banks are denoted facing downstream. Indicate on the note sheet the distance from the initial point to the edge of the water. Measure and record the depth at the edge of water. Record your start time.

6. Stand downstream from the flow meter, in a position that least affects the velocity of the water passing through the meter. Hold the rod with the meter directly facing the flow; ensuring the rod is vertical. If the stream flow is not perpendicular to the cross-section be sure to measure and record the angle coefficient using the markings on the edge of your discharge note.
7. If the depth is <2.5ft, measure velocity (V) once for each subsection at 0.6 times the total depth measured down from the water surface (e.g. if the depth = 2ft, position the torpedo at 1.2ft from the water's surface or 0.8ft from the bottom). Note that the staff is divided into tenths of a foot for easy calculation. If the depth is >2.5ft, measure V two times: at 0.2 and 0.8 times the total depth (e.g. if the depth = 3ft, measure at 0.6ft and 2.4ft from the water's surface). The average of these two readings is the V of the subsection.
8. Allow enough time between each reading (a minimum of 40 seconds for most meters) to obtain an accurate velocity. The operator calls out the distance, the depth, the velocity and the angle coefficient at each vertical. The note taker repeats back as it is recorded, as a check and balance system. For each vertical record depth, width, distance from the initial point, velocity, the observation depth (i.e. 0.2, 0.6, 0.8) and the angle coefficient (if there is one) on the discharge note. Continue this process as you move along the cross-section.
9. After measuring your last vertical record the distance from the initial point to the waters edge on the opposite bank. Record your end time.

BRIDGE BOARD AND SOUNDING REEL METHOD

1. Stretch a tape between the endpoints (width) of the bridge and mark the bridge railing permanently with a Sharpie or paint at every meter, making sure to allow for high water levels when marking. Your zero mark, or initial point, should be far enough back from the wetted edge to allow for expansion of the wetted edge during high flows. Measure the effective width (wet edge to wet edge) each time discharge is measured.
2. To obtain an accurate discharge use about 25 to 30 partial sections. With a smooth cross section and good velocity distribution, fewer sections may be used. Space the partial sections so that no partial section has more than 10 percent of the total discharge in it. The ideal measurement is one in which no partial section has more than 5 percent of the total discharge in it, but this is very seldom accomplished when 25 partial sections are used. Equal widths of partial sections across the entire cross section are not recommended unless the discharge is well distributed. Make the width of the partial sections less as depths and velocities becomes greater. Often, widths will need to be modified to accommodate for piers and other obstructions. Generally, where velocities are greater, widths are made smaller by the observer. See Appendix A for details concerning the affects of piers on width measurement.
3. Remove the meter from the protective carrying case. Check the pivot before using the meter. The point should be sharp and the pivot should be straight. If the pivot is damaged in any way replace it with the spare pivot. Check to make sure that the pivot was lubricated after the previous use. Use only one drop of oil on the pivot. See Appendix B for care and transport of current meter.
4. Perform a spin test of the bucket wheel. Holding the meter upright, with the pivot in a vertical position, spin the bucket wheel with your finger. The bucket wheel should spin, without additional help, for a minimum of two minutes before coming to rest. If the bucket wheel stops before two minutes, replace the pivot and perform another spin test. Ideally the spin test should be performed inside a vehicle or other closed space to prevent wind influence.
5. Setup the bridgeboard, sounding reel and current meter. Be sure to strap the bridge board to the bridge railing using the blue NRS strap! This is a necessary precaution to prevent accidental loss of the entire setup into the river. Use an appropriate sized sounding weight (faster velocities require heavier

weights). We have 15, 30 and 50lb sounding weights. In most cases the 15lb sounding weight will be sufficient. If the meter begins to swim from side to side in the current switch to a heavier sounding weight. Be sure to attach the meter to the marked location on the suspension rod that corresponds with the weight you are using.

6. Place the bridgeboard and sounding reel at the first interval. Lower the sounding equipment until the centerline of the bucket wheel sits at the water's surface. Reset the depth-measuring device to zero (Φ). Lower the sounding equipment to the bottom of the river and record the depth at the interval. Add the distance from the weight to the propeller assembly. For the 15 and 30lb sounding weights add 0.16m; for the 50lb sounding weight add 0.17m.
7. For each discharge measurement record the following information on the discharge note (USGS Form 9-275F):
    - Name of stream, location and site ID.
    - Date and crew
    - Time measurement was started using military time
    - Bank of stream that was the starting point
8. To ensure an accurate reading, the meter must be completely submerged under water and free of interference. Make notes about boulders, snags, pier influences or other obstructions that may bias the actual flow. Estimate the area influenced by these obstructions. Record on the field sheet which bank you begin your measurements from by writing the abbreviations LEW (left edge water) or REW (right edge water) next to that vertical. Left and right banks are denoted facing downstream. Indicate on the note sheet the distance from the initial point to the edge of the water. Measure and record the depth at the edge of water. Record your starting time.
9. After the depth is know and recorded, determine the method of velocity measurement. Normally the two-point method or the 0.6-depth method is used.

<u>The two-point method:</u>

- The two-point method is the one generally used by the US Geological Survey. This is the method we will be using for all of our verticals where the depth is greater than 0.76 m (2.5 feet). The two-point method is not used at depths less than 0.76 m (2.5 feet) because the current meter would be too close to both the water surface and the streambed to give dependable results. With the two-point method, observations of velocity are made at 0.2 and 0.8 of the depth below the water surface. The average of these two readings is the V of the subsection.

<u>Six-tenths-depth method:</u>

- With the 0.6-depth method, an observation of velocity made at 0.6 of the depth below the surface in the vertical is used as a mean velocity in the vertical. Actual observation and mathematical theory has shown that the 0.6-depth method provides reliable results and is used by the US Geological Survey under the following conditions:

    1. Whenever the depth is between 0.1 m (0.3 foot) and 0.76 m (2.5 feet).
    2. When the meter is placed a distance above the sounding weight, which makes it impossible to place the meter at the 0.8 depth. This circumstance prevents the use of the two-point method.

10. After the meter is placed at the proper depth, permit it to become adjusted to the current before starting the velocity measurement. The time required for such adjustment is usually only a few seconds if the velocities are greater than 0.3 mps, but for lower velocities, particularly if the current meter is suspended by a cable, a longer period of adjustment is needed. After the meter has become adjusted to the current, count the number of revolutions made by the rotor for a period of 40-70 seconds.
11. The operator calls out the distance, the depth, and the V. The note taker repeats back as it is recorded, as a check and balance system. For each vertical record depth, width, distance from the initial point, number of revolutions, observation depth (i.e. 0.2, 0.6, 0.8), and angle coefficient on the discharge

note. Determine the angle coefficient at each vertical by measuring the angle of the weight in relation to the riverbank using the markings on the edge of the discharge note.

12. Move to each of the verticals and repeat this procedure; record the distance from initial point, depth, meter-position depth, revolutions, and time interval, until the entire cross section has been traversed. After measuring your last vertical record the distance from the initial point to the waters edge on the opposite bank. Record your end time.
13. If the bridge is not perpendicular to the river determine an overall bridge coefficient.

Discharge Calculations

1. To obtain discharge: multiply each depth (ft or m) by the width (ft or m) of each interval, to yield the subsection area (ft^2 or m^2). Next, multiply the area by the velocity to obtain the discharge (cfs or cms) for the interval. Finally, sum all the discharge measurements across the width of the river; this will yield the total discharge of the river. If the subsection depth was >2.5ft (0.76m), then the V was taken at 0.2 and 0.8 times the total depth. Therefore, the V at 0.2 and 0.8 times the subsection depth should be averaged to yield a single V measurement before multiplying the V by the area of the subsection.
2. It is important to use the same units of measure in the field to ensure the accuracy of the flow measurements. For example, if the depth is measured in tenths, then the width should be measured in tenths for accuracy.
3. Use an Excel spreadsheet to calculate the discharge at each site. View examples from the 2002 TMDL project.

Use the following equations to calculate velocity (V):

1. For feet per second: V = 2.2048 R + 0.0178 (R=revolutions per second)*
2. For meters per second:
    - If less than 40 revolutions then: ((rev/seconds) x 2.18 + .02) x .3048 = MPS
    - If more than 40 revolutions then: ((rev/seconds) x 2.17 + .03) x .3048 = MPS

* Important: R = revolutions per second NOT the total # of revolutions.

Appendix A:

Bridges are often used for making discharge measurements of streams that cannot be waded. Measurement cross sections under bridges are often satisfactory for current-meter measurements. No set rule can be given for choosing between the upstream or downstream side of the bridge for making a discharge measurement. The advantages of using the upstream side of the bridge are:

- Hydraulic characteristics at the upstream side of bridge openings usually are more favorable.
- Approaching drift can be seen and thus can be more easily avoided.
- The streambed at the upstream side of the bridge is not likely to be scoured as badly as the downstream side.

The advantages of using the downstream side of the bridge are:

- Vertical angles are more easily measured because the sounding line will move away from the bridge.
- The flow lines of the stream may be straightened by passing through a bridge opening with piers.

Whether to use the upstream side or the downstream side of a bridge for a current-meter measurement should be decided individually for each bridge after considering the above factors. Other pertinent factors relate to physical conditions at the bridge, such as location of the walkway, traffic hazards, and accumulation of trash on pilings and piers.
Where piers are in the measuring section, it is usually necessary to use more than 25-30 subsections to obtain results as reliable as those obtained with a similar measuring section that has no piers. Piers not only affect the horizontal distribution of velocities, but they frequently affect the direction of the current, causing horizontal angles that must be carefully measured.
Whether or not to exclude the area of a bridge pier from the area of the measurement cross section depends primarily on the relative locations of the measurement section and the end of the pier. If measurements are made from the upstream side of the bridge, it is the relative location of the upstream end (nose) of the pier that is relevant; for measurements made from the downstream side it is the location of the downstream end (tail) of the pier that is relevant. If any part of the pier extends into the measurement cross section, the area of the pier is excluded. However, bridges quite commonly have cantilevered walkways from which discharge measurements are made. In that case the measurement cross section lies beyond the end of the pier-upstream from the nose or downstream from the tail, depending on which side of the bridge is used. In that situation it is the position and direction of the streamlines that determines whether or not the pier area is to be excluded. The hydrographer, if he had not previously noted the stationing of the sides of the pier when projected to the measurement cross section, does so now. If there is negligible or no downstream flow in that width interval (pier subsection)-that is, if only stagnation and (or) eddying exists upstream from the nose or downstream from the tail, whichever is relevant-the area of the pier is excluded. If there is significant downstream flow in the pier subsection, the area of the pier is included in the area of the measurement cross section. The horizontal angles of the streamlines in and near the pier subsection will usually be quite large in that circumstance.

Appendix B:

Current Meter Care and Transport

- Rinse current meter in clear water as soon as possible after use and dry using a soft cloth
- Never place a wet current meter in its carrying case
- Lubricate after 8 hours use or at least once a week when use is infrequent (see instructions)
- Always transport current meter in its protective case.

- Before placing meter in protective case raise bucket wheel with knurled brass nut to provide clearance between pivot and pivot bearing (see directions). Do not over-tighten nut as that may bend the pivot.
- After lubricating meter make sure to adjust pivot (see directions).

Appendix 5. Standard Operating Procedure for Oakton Portable Waterproof pH/CON 10 Meter Calibration

Aquatic Ecosystems Analysis Laboratory
John Muir Institute of the Environment
University of California, Davis
1490 Drew Avenue, Suite 150
Davis, CA 95616

Standard Operating Procedure for OAKTON Portable Waterproof pH/CON 10 Meter Calibration

JMIE January 2004

Purpose: This standard operation procedure (SOP) provides a detailed description for the calibration of the OAKTON Portable Waterproof pH/CON 10 Meter (Model #35630-02)

Note: All calibrations used pH/conductivity/temperature probes designed for the OAKTON Portable Waterproof pH/CON 10 Meter (Model #35630-02) only.

Step 1: Reset pH and conductivity to the factory defaults.

To reset pH, make sure the meter is in pH mode, then:

1.) While in measurement mode, press CAL/MEAS and hold for 3 seconds.
2.) The meter will prompt RST in the upper display and CAL in the lower display.
3.) Press enter to reset the meter to its factory defaults. The screen will flash all characters, then return to measurement mode once the meter is reset.

To reset conductivity, make sure the meter is in conductivity mode, and then follow steps 1-3 above.

Step 2: Preparing the pH/CON meter for calibration.

1.) Remove the protective rubber cap of the probe before calibration.
2.) Wet the probe in tap water for 10 minutes before calibrating or taking readings to saturate the pH electrode surface and minimize drift.

Step 3: 3-point (OAKTON pH 4.00, 7.00 and 10.00) pH calibration.

1.) If necessary, press the MODE key to select pH mode. The pH indicator appears in the upper right hand corner of the display.
2.) Rinse the probe thoroughly with de-ionized water or a rinse solution. Do not wipe the probe; this causes a build-up of electrostatic charge on the glass surface.
3.) Dip the probe into the calibration buffer. The end of the probe must be completely immersed into the sample. Stir the probe gently to create a homogenous sample.
4.) Wait for the measured pH value to stabilize. The READY indicator will display when the reading stabilizes.
5.) Press CAL/MEAS to enter pH calibration mode. The primary display will show the measured reading, while the smaller secondary display will indicate the pH standard buffer solution. Scroll up or down until the secondary display value is the same as the pH buffer value you are using (pH 4.00, 7.00 or 10.00).

6.) Wait for the measured pH value to stabilize. The READY indicator will display when the reading stabilizes.
7.) After the READY indicator turns on, press ENTER to confirm calibration. A confirming indicator (CON) flashes and disappears. The meter is now calibrated at the buffer indicated in the secondary display.
8.) The secondary display automatically scrolls to the next buffer calibration option. Scroll up or down to select the next buffer value you want to calibrate (pH 4.00, 7.00 or 10.00).
9.) Rinse the probe with de-ionized water or a rinse solution, and place it in the next pH buffer.
10.) Follow steps 5-8 for additional calibration points.
11.) When calibration is complete, press CAL/MEAS to return to pH measurement mode.

Note: If the selected buffer value is not within +/-1.00 pH from the measured value: the electrode and buffer icon blink and the ERR annunciator appears in the lower left corner of the display. These indicators also flash if the buffer used in not the same as the buffer value on the secondary display.

Step 4: Conductivity Calibration

1.) Pour out two separate portions of the calibration standard and one of deionized water into separate clean containers. Choose a calibration solution value that is approximately 2/3 the full-scale value of the measurement range (e.g. in the 0 to 1999 µS range, use a 1413 µS solution for calibration). A 447 µS standard solution is generally adequate in this study.
2.) If necessary, press the MODE key to select the Conductivity Mode. The µS or mS indicator will appear on the right side of the display.
3.) Rinse your probe with deionized water, then rinse the probe in one of the portions of calibration standard.
4.) Immerse the probe into the second portion of calibration standard. The meter's autoranging function selects the appropriate conductivity range (four ranges are possible). Be sure to tap the probe to remove air bubbles. Air bubbles will cause errors in calibration.
5.) Wait for the reading to stabilize. The READY indicator lights when the reading is stable.
6.) Press the CAL/MEAS key. The CAL indicator appears above the primary display. The primary display shows the factory default and the secondary display shows the temperature.
7.) Scroll up or down to the value of your conductivity standard. Press and hold the scroll keys to go faster. The meter automatically compensates for temperatures using a factor of 2.00% per C.
8.) Press the ENTER key to confirm calibration. Upon calibration, the CON indicator appears briefly. The meter automatically switches back into Measurement mode. The display now shows the calibrated, temperature compensated conductivity value.

9.) For calibration in other ranges (Maximum: 4 ranges) repeat steps 1 through 9 with the appropriate calibration standards.

Note: if the calibration value input into the meter is different from the factory default value displayed by more than 30%, the ERR annunciator appears in the lower left corner of the display. Clean probe with alcohol. Verify that your calibration standard is fresh and accurate.

Step 5: Calibration Documentation

1.) After calibrating a meter for pH and conductivity, the person who calibrated the meter will record the date, which calibrations were made and their initials on a decal affixed to the inside of the meter case.

*Steps were transposed from the OAKTON Portable Waterproof pH/CON 10 Meter (Model #35630-02) manual of operating instructions (68X230403 rev2 01 / 02).

Appendix 6. Determination of Organophosphorous Pesticides in Water Samples

Determination of Organophosphorous Pesticides in Water Samples

1.0 Scope and Application

1.1 This is a modified EPA Method 8141A and describes the sample preparation and quantitative analysis of trace level organophosphorous pesticides in surface, municipal and wastewater using liquid-liquid extraction and high resolution gas chromatography with Flame Photometric Detector (FPD) in phosphorous mode and Thermionic Bead Specific Detector (TSD). The following target analytes can be determined by this method:

Target Analyte	CAS Registry No.
Aspon	3244-90-4
Azinphos ethyl	2642-71-9
Azinphos methyl	86-50-0
Bolstar (Sulprofos)	35400-43-2
Carbophenothion	786-19-6
Chlorfenvinphos	470-90-6
Chlorpyrifos	2921-88-2
Chlorpyrifos methyl	5598-13-0
Ciodrin (Crotoxyphos)	7700-17-6
Coumaphos	56-72-4
Demeton-s	126-75-0
Diazinon	333-41-5
Dichlofenthion	97-17-6
Dichlorvos	62-73-7
Dicrotophos	141-66-2
Dimethoate	60-51-5
Dioxathion	78-34-2
Disulfoton	298-04-4
Ethion	563-12-2
Ethoprop	13194-48-4
Famphur	52-85-7
Fenchlorphos (Ronnel)	299-84-3
Fenitrothion	122-14-5
Fensulfothion	115-90-2
Fenthion	55-38-9
Fonofos (Dyfonate)	944-22-9
Leptophos	21609-90-5
Malathion	121-75-5
Merphos	150-50-5

Methidathion	950-37-8
Mevinphos (Phosdrin)	7786-34-7
Molinate	2212-67-1
Naled (Dibrom)	300-76-5
Parathion, Ethyl	56-38-2
Parathion, Methyl	298-00-0
Phorate	298-02-2
Phosmet	732-11-6
Phosphamidon	13171-21-6
Sulfotep	3689-24-5
Terbufos	13071-79-9
Tetrachlorvinphos	22248-79-9
Thiobencarb	28249-77-6
Thionazin	297-97-2
Tokuthion	34643-46-4
Trichlorfon	52-68-6
Trichloronate	327-98-0
Triphenyl phosphate (surrogate)	115-86-6

1.2 The estimated detection limit for each analyte is listed in Table 1. The actual MDL may differ from those listed, depending upon the nature of interferences in the sample matrix. Validation of the target analytes produced recoveries greater than 70 percent (Appendix I) for most analytes. Some target compounds are widely accepted as having lower recoveries, as listed in Section 9.3.3. The range of percent recoveries for each analyte is also included in Table 1.

1.3 If possible, unknowns in the sample will be qualitatively confirmed for compound identification by Gas Chromatography with a Mass Spectrometer – Ion Trap Detector (GC/MS-ITD).

Table 1. Organophosphorous pesticides analyzed, their Minimum Detection Limits (MDL), Reporting Limits (RL) and Range of Percent Recovery in water.

Target Analytes	MDL (µg/l)	RL (µg/l)	Recovery Range (%)*
Aspon	0.030	0.050	85 – 105
Azinphos ethyl	0.030	0.050	95 – 110
Azinphos methyl (Guthion)	0.030	0.050	50 – 90
Bolstar (Sulprofos)	0.030	0.050	80 – 95
Carbophenothion	0.030	0.050	90 – 100
Chlorfenvinphos	0.030	0.050	80 – 100
Chlorpyrifos	0.020	0.050	80 – 100
Chlorpyrifos methyl	0.020	0.050	95 – 110
Ciodrin (Crotoxyphos)	0.030	0.050	90 – 110

Coumaphos	0.040	0.050	50 – 90
Demeton-s	0.040	0.050	30 – 80
Diazinon	0.005	0.020	95 – 110
Dichlofenthion	0.030	0.050	95 – 105
Dichlorvos	0.030	0.050	85 – 105
Dicrotophos	0.030	0.050	20 – 70
Dimethoate	0.030	0.050	90 – 100
Dioxathion	0.030	0.050	50 – 90
Disulfoton	0.010	0.050	80 – 95
Ethion	0.020	0.050	80 – 105
Ethoprop	0.030	0.050	80 – 100
Famphur	0.030	0.050	90 – 105
Fenchlorphos (Ronnel)	0.030	0.050	90 – 105
Fenitrothion	0.030	0.050	90 – 110
Fensulfothion	0.030	0.050	40 – 80
Fenthion	0.030	0.050	80 – 100
Fonofos (Dyfonate)	0.020	0.050	85 – 110
Leptophos	0.030	0.050	80 – 100
Malathion	0.030	0.050	95 – 105
Merphos	0.030	0.050	85 – 110
Methidathion	0.030	0.050	95 – 105
Mevinphos (Phosdrin)	0.030	0.050	80 – 90
Molinate	0.100	0.200	65 – 100
Naled (Dibrom)	0.030	0.050	40 – 80
Parathion, Ethyl	0.030	0.050	85 – 110
Parathion, Methyl	0.010	0.050	90 – 105
Phorate	0.030	0.050	80 – 95
Phosmet	0.030	0.050	80 – 100
Phosphamidon	0.030	0.050	85 – 100
Sulfotep	0.030	0.050	95 – 110
Terbufos	0.030	0.050	85 – 100
Tetrachlorvinphos	0.030	0.050	80 – 105
Thiobencarb	0.100	0.200	90 – 110
Thionazin	0.040	0.050	95 – 110
Tokuthion	0.030	0.050	85 – 105
Trichlorfon	0.030	0.050	90 – 115
Trichloronate	0.030	0.050	80 – 105
Triphenyl phosphate (surrogate)	0.030	0.050	90 – 105

* Recoveries fall within 75-125% accept as discussed in Section 9.3.3.

2.0 Summary of Method

2.1 A measured volume of sample (1000 ml) is extracted with methylene chloride (DCM) using a separatory funnel. The DCM extract is dried with sodium sulfate, evaporated using Kuderna-Danish (K-D) and solvent exchanged into petroleum ether. The extract is concentrated with micro-snyder (micro K-D) apparatus to approximately 1 ml and adjusted to 2.0 ml with iso-octane. The extracts are analyzed by gas chromatography using conditions which permit the separation and measurement of the target analytes in the extracts by FPD and TSD detection.

2.2 Interferences in analyses may be encountered in very dirty samples and cleanup may be needed to aid in the elimination or reduction of these interferences. Florisil column cleanup or Gel Permeation Chromatography (GPC) procedures will be followed.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may cause GC artifacts and/or elevated baselines, resulting in the misinterpretation of chromatograms. All materials should be demonstrated to be free from interferences under the conditions of the analysis by running method blanks initially and with each sample lot. Specific selection of reagents and purification of solvents by distillation in all-glass systems are required. High-purity distilled-in-glass solvents are commercially available.

An effective way of cleaning laboratory glassware is by rinsing with polar and non-polar solvents before use. The cleaning procedure used must be tested by analyzing procedural blanks prior to analyzing samples.

3.2 Phthalates are common laboratory contaminants that are used widely as plasticizers. Sources of phthalate contamination include plastic lab-ware, plastic tubing, plastic gloves, plastic coated glassware clamps, and have been found as a contaminant in Na_2SO_4.

Polytetrafluoroethylene (PTFE) can be used instead of polypropylene or polyethylene to minimize this potential source of contamination. However, use of PTFE lab-ware will not necessarily preclude all phthalate contamination. Na_2SO_4 can be solvent rinsed to eliminate contaminants.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source. A Florisil or GPC cleanup procedure can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4.0 Apparatus and Laboratory Supplies

4.1 Separatory funnel. 2000-ml, with TFE-fluorocarbon stopcock, ground glass or TEF stopper.

4.2 Automatic shaker designed to fit 2 liter separatory funnels with rpm and timer controls.

4.3 Beakers. Borosilicate glass, 400 mL

4.4 Chromatographic Column. 300 cm x 22 cm borosilicate glass chromatography column with Teflon stopcock.

4.5 Glass wool. Pyrex - solvent washed prior to use.

4.6 Kuderna-Danish (K-D) Apparatus.

4.6.1 Concentrator tube. 15 mL, graduate (Kontes K0570012-0500, or equivalent). A ground stopper, 19/22 joint, is used to prevent evaporation of extracts.

4.6.2 Evaporation flask. 500 mL (Kontes K-570050-0500, or equivalent), attached to concentrator tube with blue clamp (Kontes K-662750-0012).

4.6.3 Snyder column. Three ball (Kontes K-503000-0121, or equivalent).

4.6.4 Micro-Snyder column. Alltech 9058 or equivalent.

4.6.5 Boiling chips. Hengar granules, high purity amphoteric alundum - extracted with acetone and petroleum ether. Note that boiling chips can be a significant source of contamination if not properly cleaned.

4.7 Water bath. Blue M, 115 V, thermostatically controlled with stainless steel cover to fit K-D apparatus, installed in a fume hood.

4.8 GC vials. GC autosampler vials, borosilicate glass, 2 mL with PTFE-lined screw cap.

4.9 Analytical balance. Capable of weighing 0.1 mg.

4.10 Drying oven.

4.11 Disposable Pasteur Pipettes. 2 mL, rinsed with solvents before use.

4.12 Glass filter funnel. Fluted, 75 mm or larger.

4.13 Graduated cylinder. 1000 ml, 250 mL and 100 mL.

4.14 Culture tubes. 13 x 100 mm with PTFE lined screw cap.

4.15 Analytical systems

4.15.1 Gas chromatograph. **Agilent 6890** equipped with dual FPD detectors with phosphorous filters, split-splitless injector in pulsed splitless mode with EPC, a **7683** autosampler and dual capillary columns (J&W Scientific) connected to a single injection port using a "Y" press fit connector. Section 9 describes the acquisition and analysis procedures while Table 2 lists the operating parameters.

4.15.2 Gas chromatograph. **Varian 3600**, equipped with dual Thermionic Specific Detectors (TSD), direct and Septum Programmable Injector (SPI), a **8200** autosampler and dual megabore columns (J&W Scientific). Section 9 describes the acquisition and analysis procedures while Table 3 lists the operating parameters.

4.15.3 Data System. Hewlett-Packard, to collect and record GC data, generates reports, computes and records response factors for multi-level calibrations. Data system should be capable of calibrating a method using a minimum of 5 concentrations of analytical standards and calculating in external standard mode.

Table 2 Operating parameters for Agilent 6890 GC/FPD

Gases
Carrier: Helium, 1 mL/min
Makeup: Nitrogen, 1 mL/min
Flame: Air and Hydrogen

Columns
DB5, 30 m x 0.32 mm I.D. x 0.25 µm film thickness
DB17, 30 m x 0.32 mm I.D. x 0.25 µm film thickness

Inlet
Isocratic temp: 200 ºC

Oven
Initial temperature: 90 ºC Initial time: 1.00 min
Ramp 1: 8.0 deg/min, final temp 220 ºC, hold time 5.00 min
Ramp 2: 20.0 deg/min, final temp 250 ºC, hold time 13.00 min

Detectors (FPD)
Temperature: 225 ºC

Injection Volume: 3 µL

Table 3 Operating parameters for Varian 3600 GC/TSD

Gases
Carrier: Helium
Makeup: Nitrogen
Flame: Air and Hydrogen

Columns
DB5, 15 m x 0.53 mm I.D. x 1.5 µm film thickness
DB17, 15 m x 0.53 mm I.D. x 1.5 µm film thickness

Inlet
Isocratic temp: 190 ºC

Oven

Initial temperature: 190 ºC Initial time: 3.00 min
Ramp 1: 5.0 deg/min, final temp 250 ºC, hold time 10.00 min

Detectors (TSD)
Temperature: 225 ºC

Injection Volume: 3 µL

5.0 Reagents, materials, gases and standards

5.1 Reagent water is defined as water in which an interferent is not observed at method detection limit of each parameter of interest. Deionized (DI) water was used for method validation and as method blank.

5.2 Petroleum ether (PE), acetone, methylene chloride (DCM), diethyl ether, isooctane. Pesticide residue quality or equivalent.

5.3 Sodium sulfate. Anhydrous granular reagent grade, rinsed with PE prior to use.

5.4 Nitrogen. Ultra-pure (99.99999%) for GC/FPD/TSD

5.5 Helium. Ultra-pure (99.99999%) for GC/FPD/TSD

5.6 Air. Compressed, breathing quality for GC/FPD/TSD

5.7 Hydrogen. Ultra high purity for GC/FPD/TSD

5.8 Stock standards. Individual stock standards (100 µg/ml) are purchased as certified solutions from ChemService as well as premixed solutions of 8140 and 8141A, as shown in Table 4. Additional compounds analyzed are prepared as WPCL solution "OP Mix C"

Table 4 Organophosphorous analyte spiking solutions and standard curves.

EPA 8140 Analytes	EPA 8141A Analytes	OP Mix C Analytes
Azinphos methyl(Guthion)	Aspon	Dimethoate
Bolstar (Sulprofos)	Azinphos ethyl	Malathion
Chlorpyrifos	Carbophenothion	Methidathion
Coumaphos	Chlorfenvinphos	Molinate
Demeton-s	Chlorpyrifos methyl	Parathion,Ethyl
Diazinon	Ciodrin (Crotoxyphos)	Sulfotep
Dichlorvos	Dichlofenthion	Thiobencarb
Disulfoton	Dicrotophos	
Ethoprop (Prophos)	Dioxathion	
Fenchlorphos (Ronnel)	Ethion	
Fensulfothion	Famphur	

Fenthion	Fenitrothion
Merphos	Fonofos (Dyfonate)
Mevinphos (Phosdrin)	Leptophos
Naled (Dibrom)	Phosmet (Imidan)
Parathion, Methyl	Phosphamidon
Phorate	Terbufos
Tetrachlorvinphos	Thionazin (Zinophos)
Tokuthion	Trichlorfon (Dylox)
Trichloronate	

6.0 Sample Collection, Preservation, and Storage

6.1 Samples are collected in one liter amber glass bottles and iced or refrigerated at 4 °C from time of collection until extraction.

6.2 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction.

7.0 Sample Extraction

7.1 Remove water samples from refrigerator and transfer contents to a pre-cleaned 2-liter separatory funnel. Immediately add 1.0 ml of the 200 ppb OP pesticide surrogate solution to every sample. For Method Blank, add 1.0 ml of the 200 ppb OP pesticide surrogate solution (TPP) to 1 liter DI water. For laboratory control spike (LCS) and matrix spikes (MS/MSD) also add 1.0 ml of 200 ppb OP pesticide spiking solution for each mix (8140, 8141A and Mix C)

7.2 Add 60 ml of methylene chloride (DCM) to the empty bottle, replace the cap and rinse the bottle. Pour the DCM into the separatory funnel and repeat with another 60 mL aliquot of DCM. Extract the sample by shaking the funnel for 5 minutes on the auto-shaker with periodic venting to release excess pressure. Allow organic layer to separate from the water phase for a minimum of 10 minutes. Collect the methylene chloride extract in a 400 ml beaker.

7.3 Add a second 120 ml volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the beaker.

7.4 Set up and label pre-cleaned K-D flasks with concentrator tubes and attached with a blue clamp on ring stands in the fume hood. Add 0.5 ml iso-octane as "keeper" and a solvent rinsed micro-boiling chip to each K-D concentrator tube. Place a filter funnel containing a plug of pre-cleaned glass wool in the bottom of the funnel and place the funnel in the top of the K-D flask. Add about two inches of solvent rinsed sodium sulfate to the funnel.

7.5 Pour the combined extracts from the beaker through sodium sulfate into the K-D flask. Rinse the beaker with about 10 mL of DCM and add this rinse to the sodium sulfate. Repeat with another 10 mL DCM rinse. Rinse the sodium sulfate with an additional portion of DCM (~10-20 mL).

7.6 Place a Snyder column on the K-D flask, clamp with a green clamp and place the flask on the hot water bath set at 78-82 ^{o}C. Evaporate solvent on the hot water bath. When the apparent volume of solvent in the concentrator tube is 5-10 mL, add 20-30 mL of petroleum ether through the top of the Snyder column. Repeat this procedure when the apparent volume is again at 5-10 mL. When the reflux line falls below the top of the Snyder column, the K-D apparatus should be removed

from the hot water bath. Dry outer KD apparatus with a Kimwipe to prevent condensation water from entering the concentrator tube. Upon cooling, remove the concentrator tube from the K-D apparatus.

7.7 Place a clean micro-Snyder column on the concentrator tube with a blue clamp, add a new micro boiling chip and place in a 400 mL beaker containing water heated to approximately 78 ^{o}C on a hot plate. If the solvent does not begin to boil, remove the tube from the bath immediately, allow it to cool slightly, add a new micro boiling stone to prevent it from bumping and place it back in the bath.

7.8 When the solvent has been evaporated to 0.5-1 mL remove the tube from the bath and allow it to cool in a test tube rack. Dry outer KD apparatus with a Kimwipe to prevent condensation water from entering the concentrator tube. Remove the micro-Snyder column and add iso-octane to the concentrator tube to reach a final volume of 2.0 mL. Mix the tube contents by tapping the bottom of the tube causing a vortex which will rinse the sides of the tube. A Vortex Genie mixer may be used for this step.

7.9 Transfer the solution from the concentrator tube to a culture tube and cap with a Teflon faced cap. Place extracts in a refrigerator for storage until analysis or cleanup, if necessary.

7.10 When ready for analysis, transfer extract to labeled GC vials and cap.

8.0 Cleanup Procedure

8.1 Cleanup of dirty samples may be necessary due to interferences in the analysis of baseline or co-elution with target analytes of the sample extract. Follow the in-house SOP for Florisil® column or GPC method, as needed.

9.0 Analytical Procedure

9.1 The final extract will be analyzed on an Agilent 6890 GC/FPD and a Varian 3600 GC/TSD.

9.1.1 Chromatographic conditions for operating the Agilent 6890 GC/FPD are found in Table 2

9.1.2 Chromatographic conditions for operating the Varian 3600 GC/TSD are found in Table 3.

9.2 GC acquisition

9.2.1 Pour several isooctanes into GC vials using the same lot as used for samples with each GC run.

9.2.2 Pour standard curves into GC vials using 20, 50, 100, 200 and 500 ppb Std 8140 and 8141A and 50, 100, 200 and 500 ppb OP Mix C in isooctane. Pour extra vials of a midlevel concentration for use as CCV (to be analyzed every 20 samples or less).

9.2.3 Create sequence file and sequence table on computer. Use the WPCL login number for “Data Subdirectory” and “Save As” sequence name.

9.2.4 Acquire data and recap each vial daily to preserve sample integrity.

9.3 Analysis

9.3.1 Recalibrate OP curves and analyze samples in external standard mode. Add a printed chromatogram and report for each standard and sample to folder.

9.3.2 Certain analytes will coelute on a given column. However, using two columns with different polarities will allow for confirmation of target analytes.

9.3.3 EPA Method 8141A cites the following common analytical difficulties encountered for target analytes:

9.3.3.1 The water solubility of Dichlorvos (DDVP) is 10 g/L at 20EC, and recovery is poor from aqueous solution.

9.3.3.2 Naled is converted to Dichlorvos (DDVP) on column by debromination. This reaction may also occur during sample workup. The extent of debromination will depend on the nature of the matrix being analyzed. The analyst must consider the potential for debromination when Naled is to be determined.

9.3.3.3 Trichlorfon rearranges and is dehydrochlorinated in acidic, neutral, or basic media to form Dichlorvos (DDVP) and hydrochloric acid. If this method is to be used for the determination of organophosphates in the presence of Trichlorfon, the analyst should be aware of the possibility of rearrangement to Dichlorvos to prevent misidentification.

9.3.3.4 Demeton (Systox) is a mixture of two compounds; O,O-diethyl O-[2-(ethylthio)ethyl]phosphorothioate (Demeton-O) and O,O-diethyl S-[2-(ethylthio)ethyl]phosphorothioate (Demeton-S). Two peaks are observed in all the chromatograms corresponding to these two isomers. It is recommended that the early eluting compound (Demeton-S) be used for quantitation.

9.3.3.5 Dioxathion is a single-component pesticide. However, several extra peaks are observed in the chromatograms of standards. These peaks appear to be the result of spontaneous oxygen-sulfur isomerization. Because of this, Dioxathion is not included in composite standard mixtures.

9.3.3.6 Merphos (tributyl phosphorotrithioite) is a single-component pesticide that is readily oxidized to its phosphorotrithioate (Merphos oxone). Chromatographic analysis of Merphos almost always results two peaks (unoxidized Merphos elutes first). As the relative amounts of oxidation of the sample and the standard are probably different, quantitation based on the sum of both peaks may be most appropriate.

9.3.3.7 Many analytes will degrade on reactive sites in the chromatographic system. Analysts must ensure that injectors and splitters are free from contamination and are silanized. Columns should be installed and maintained properly.

9.3.3.8 Performance of chromatographic systems will degrade with time. Column resolution, analyte breakdown and baselines may be improved by column washing. Oxidation of columns is not reversible.

10.0 References

U.S. Environmental Protection Agency, Office of Water, EPA 821-R-92-002, April 1992, Methods For The Determination of Nonconventional Pesticides In Municipal And Industrial Wastewater, p. 227.
Method 622, *The Determination of Organophosphorous Pesticides in Municipal and Industrial Wastewater*.
Method 8141A, Organophosphorous Compounds by Gas Chromatography: Capillary Column Technique.
Method 622, *The Determination of Organophosphorous Pesticides in Municipal and Industrial Wastewater*.
Method 8141A, *Organophosphorous Compounds by Gas Chromatography: Capillary Column Technique.*

Appendix 7. Determination of Carbamate Pesticides in Water Samples

Determination of Carbamate Pesticides in Water Samples

1.0 Scope and Application

1.1 This is a modified EPA Method 632 and describes the sample preparation and quantitative analysis of trace level carbamate pesticides in surface, municipal and wastewater using liquid-liquid extraction and a liquid chromatography quadropole system (LC-MSD) coupled to a diode array UV-Vis detector (DAD).

1.2 The estimated detection limit for each analyte is listed in Table 1. The actual MDL may differ from those listed, depending upon the nature of interferences in the sample matrix. Validation of the target analytes produced recoveries greater than 65 percent for most analytes.

Table 1. Carbamate pesticides analyzed, their Minimum Detection Limits (MDL) and Reporting Limits (RL) in water.

Target Analytes	MDL (µg/l)	RL (µg/l)
Aldicarb	0.010	0.020
Captan	0.050	0.100
Carbaryl	0.010	0.020
Carbofuran	0.010	0.020
Diuron	0.002	0.005
Linuron	0.002	0.005
Methiocarb	0.150	0.250
Methomyl	0.010	0.020

2.0 Summary of Method

2.1 A measured volume of sample (1000 ml) is extracted with methylene chloride (DCM) using a separatory funnel. The DCM extract is dried with sodium sulfate, concentrated and solvent exchanged by rotary evaporation and adjusted to 2.0 ml with acetonitrile. The extracts are analyzed by liquid chromatography using conditions which permit the separation and measurement of the target analytes in the extracts by MSD detection.

2.2 Interferences in analyses may be encountered in very dirty samples and cleanup may be needed to aid in the elimination or reduction of these interferences. Gel Permeation Chromatography (GPC) cleanup procedures will be followed.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may cause LC artifacts and/or elevated baselines, resulting in the misinterpretation of chromatograms. All materials should be demonstrated to be free from interferences under the conditions of the analysis by running method blanks initially and with each sample lot. Specific selection of reagents and purification of solvents by distillation in all-glass systems are required. High-purity distilled-in-glass solvents are commercially available.

An effective way of cleaning laboratory glassware is by rinsing with polar and non-polar solvents before use. The cleaning procedure used must be tested by analyzing procedural blanks prior to analyzing samples.

3.2 Phthalates are common laboratory contaminants that are used widely as plasticizers. Sources of phthalate contamination include plastic lab-ware, plastic tubing, plastic gloves, plastic coated glassware clamps, and have been found as a contaminant in Na_2SO_4.

Polytetrafluoroethylene (PTFE) can be used instead of polypropylene or polyethylene to minimize this potential source of contamination. However, use of PTFE lab-ware will not necessarily preclude all phthalate contamination. Na_2SO_4 can be solvent rinsed to eliminate contaminants.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source. GPC cleanup procedure can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4.0 Apparatus and Laboratory Supplies

4.1 Separatory funnel. 2000-ml, with TFE-fluorocarbon stopcock, ground glass or TEF stopper.

4.2 Automatic shaker designed to fit 2 liter separatory funnels with rpm and timer controls.

4.3 Beakers. Borosilicate glass, 400 mL

4.4 Graduated cylinder. 1000 ml, 250 mL and 100 mL.

4.5 Glass wool. Pyrex - solvent washed prior to use.

4.6 Evapotec rotary film evaporator.

4.7 GC vials. GC autosampler vials, borosilicate glass, 2 mL with PTFE-lined screw cap.

4.8 Analytical balance. Capable of weighing 0.1 mg.

4.9 Drying oven.

4.10 Disposable Pasteur Pipettes. 2 mL, rinsed with solvents before use.

4.11 Glass filter funnel. Fluted, 75 mm or larger.

4.12 Culture tubes. 13 x 100 mm with PTFE lined screw cap.

4.13 Analytical systems

4.13.1 LC-MSD chromatograph. Analysis was performed using an Agilent 1100 series LC-MS quadrupole system coupled to an Agilent 1100 series LC system consisting of a binary pump, diode array UV-Vis detector (DAD), autosampler, thermostated column compartment and vacuum degasser. The DAD was used to assist with method development, confirmation and troubleshooting. The MS was operated with atmospheric pressure electrospray ionization (API-ES) source in positive ion mode.

Section 9 describes the acquisition and analysis procedures while Table 2 lists the operating parameters.

4.13.2 Data System. Hewlett-Packard, to collect and record GC data, generates reports, computes and records response factors for multi-level calibrations. Data system should be capable of calibrating a method using a minimum of 5 concentrations of analytical standards and calculating in external standard mode.

Table 2 Operating parameters for Agilent 1100 LC-MSD

Chromatographic Conditions
- Column: Agilent Zorbax C-18 column, 15cm x 4.6mm i.d. x 5µm (or equivalent)
- Mobile phase A: water (5mM formic acid)
- Mobile phase B: acetonitrile (5mM formic acid)
- Pump parameters: gradient from 5% to 100% Acetonitrile in 25 min.
- Flow rate: 1.0 ml/min
- Run time: 35 minutes
- Column temperature: 38ºC
- Injection volume: 20 µL
- Diode array detector (DAD):

Signal,	Bw (nm)	Reference,	Bw (nm)
254	16	400	8
245	16	400	8

MS Conditions: API-ES in positive ion mode
- Drying gas flow: 12 L/min
- Drying gas temperature: 350ºC
- Nebulizer gas pressure: 40 psig
- Capillary voltage: 3000
- Fragmentor voltage: 140
- Selected ion monitoring (SIM): multi-ions (see analytical method for details)
- Scan: m/z 100-350
- Threshold: 150 counts
- Gain: 2
- Step size: 0.1 amu
- Peak width: 0.1 min
- Time filter: On

5.0 Reagents, materials, gases and standards

5.1 Reagent water is defined as water in which an interferent is not observed at method detection limit of each parameter of interest. Deionized (DI) water was used for method validation and as method blank.

5.2 Petroleum ether (PE), acetone, acetonitrile, methylene chloride (DCM), diethyl ether, isooctane. Pesticide residue quality or equivalent.

5.3 Sodium sulfate. Anhydrous granular reagent grade, rinsed with PE prior to use.

5.4 Liquid Nitrogen. 230 psi or higher.

5.5 Stock standards. Individual stock standards (100 µg/ml) are purchased as certified solutions from ChemService.

6.0 Sample Collection, Preservation, and Storage

6.1 Samples are collected in one liter amber glass bottles and iced or refrigerated at 4 °C from time of collection until extraction.

6.2 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction.

7.0 Sample Extraction

7.1 Remove water samples from refrigerator and transfer contents to a pre-cleaned 2-liter separatory funnel. For laboratory control spike (LCS) and matrix spikes (MS/MSD) add 1.0 ml of 200 ppb carbamate spiking solution.

7.2 Add 60 ml of methylene chloride (DCM) to the empty bottle, replace the cap and rinse the bottle. Pour the DCM into the separatory funnel and repeat with another 60 mL aliquot of DCM. Extract the sample by shaking the funnel for 5 minutes on the auto-shaker with periodic venting to release excess pressure. Allow organic layer to separate from the water phase for a minimum of 10 minutes. Collect the methylene chloride extract in a 400 ml beaker.

7.3 Add a second 120 ml volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the beaker.

7.4 Set up and label pre-cleaned round bottom flasks. Add 0.5 ml acetonitrile as “keeper”. Place a filter funnel containing a plug of pre-cleaned glass wool in the bottom of the funnel and place the funnel in the top of the round bottom flask. Add about two inches of solvent rinsed sodium sulfate to the funnel.

7.5 Pour the combined extracts from the beaker through sodium sulfate into the round bottom flask. Rinse the beaker with about 10 mL of DCM and add this rinse to the sodium sulfate. Repeat with another 10 mL DCM rinse. Rinse the sodium sulfate with an additional portion of DCM (~10-20 mL).

7.6 Concentrate to almost dry with rotary evaporator in water bath (36ºC). Bring to final volume of 2 mL acetonitrile. Filter with 0.45 µm Gelman filter into vial.

8.0 Cleanup Procedure

8.1 Cleanup of dirty samples may be necessary due to interferences in the analysis of baseline or co-elution with target analytes of the sample extract. Follow the in-house SOP for GPC method, as needed.

9.0 Analytical Procedure

9.1 The final extract will be analyzed on an Agilent 1100 LC-MSD. Conditions for operating the Agilent 1100 LC-MSD are found in Table 2.

Appendix 8. Diquat and Paraquat in water (C_8 cartridge)by LC-MSD

1.0 Reagent and Buffer Solutions

a. Conditioning solution A: Dissolve 0.500 g of cetyl trimethyl ammonium bromide and 5 ml of concentrated ammonium hydroxide in 500 ml of deionized water and dilute to 1000 ml in volumetric flask.

b. Conditioning solution B: Dissolve 10.0 g of 1-hexanesul-fonic acid, sodium salt and 10 ml of concentrated ammonium hydroxide in 250 ml deionized water and dilute to 500 ml in volumetric flask.

c. Sodium hydroxide solution, 10% w/v: Dissolve 50 g of sodium hydroxide into 400 ml of deionized water and dilute to 500 ml in volumetric flask.

d. Hydrochloric acid, 10% v/v: Add 50 ml of concentrated hydrochloric acid to 400 ml of DI water and dilute to 500 ml in a volumetric flask.

e. Disk or cartridge eluting solution: Add 13.5 ml of orthophosphoric acid and 10.3 ml of diethylamine to 500 ml of deionized water and dilute to 1000 ml in volumetric flask.

f. Ion-pair concentrate: Dissolve 3.75 g of 1-hexanesul-fonic acid in 15 ml of the disk or cartridge eluting solution and dilute to 25 ml in volumetric flask with the disk eluting solution.

g. Buffer solution: Dissolve 3.5 ml of triethylamine and 1.0 g of 1-hexane-sulfonic acid sodium salt in 500 ml HPLC water. Adjust pH 2.5 with phosphoric acid (1.0-2.0 ml) and dilute to 1000 ml in volumetric flask. Filter first through 0.45 μm, then through 0.20 μm.

All chemical supply from Aldrich company.

2.0 Solid Phase Extraction

Before sample extraction, the C_8 extraction cartridges (Supelclean™ LC-8, 6 mL, 0.5g) must be conditioned by the following procedure.

a. Elute the following solutions through the cartridge in the stated order. Take special care not to let the column go dry. The flow rate through the cartridge should be approximately 10 ml/min.
   Deionized water, 5 ml
   Methanol, 5 ml
   Deionized water, 5 ml
   Conditioning solution A, 5 ml
   Deionized water, 5 ml
   Methanol, 10 ml
   Deionized water, 5 ml
   Conditioning solution B, 10 ml

b. Retain conditioning solution B in the C_8 cartridge to keep it activated.

c. Measure a 500 ml aliquot of the sample.

d. Filter samples through Whatman filter paper (filter # 4, 2 or 5) if necessary.

e. Immediately before extraction, adjust the pH of the sample to 10.5 ± 0.2 with 10% w/v NaOH (aq) or 10% v/v HCl (aq). It's about 23-25 drops of 10% NaOH for DI water pH 7.0

f. Filter sample through glass microfiber filter 1.2 µm.

g. Attach a 60 ml reservoir to the conditioned C_8 cartridge. Turn on the vacuum pump and adjust the flow rate to 3-6 ml/min. Filter the sample through the cartridge. DO NOT LET COLUMN GO DRY. Wash the column with 5 ml of HPLC grade methanol. Continue to draw the vacuum through the cartridge for one additional minute to dry the cartridge. Release the vacuum and discard the waste.

h. Align cartridges with 13 mm culture tubes in a dry vacuum box and add 4.5 ml of the eluting solution to the sample cartridge. Turn on the vacuum and adjust the flow rate to 1-2 ml/min.

i. Fortify the extract with 100 µL of the ion-pair concentrate. Adjust the volume to the mark with eluting solution, mix thoroughly, and seal tightly until analyzed.

j. Filter sample through 0.45 µm to the vial before analyzed.

3.0 LC-MS Conditions

Instrument: Agilent LC-MSD 1100 equipped with DAD, auto sampler, and data system.

Chromatographic Conditions

- Column: Waters Atlantis dC-18 column, 10cm x 2.1mm i.d. x 3µm
- Mobile phase A: 5mM tridecafluoroheptanoic acid (TDFHA)
- Mobile phase B: acetonitrile
- Pump parameters: isocratic A: 75% B: 25%
- Flow rate: 0.35 ml/min
- Run time: 17 minutes
- Column temperature: 36ºC
- Injection volume: 20 µL
- Diode array detector (DAD):

Signal,	Bw (nm)	Reference,	Bw (nm)	
308	4	400	8	Diquat
257	4	400	8	Paraquat

MS Conditions: API-ES in positive ion mode

- Drying gas flow: 12 L/min
- Drying gas temperature: 350ºC
- Nebulizer gas pressure: 40 psig
- Capillary voltage: 3000
- Fragmentor voltage: 90
- Selected ion monitoring (SIM): m/z 183.0 (Diquat), m/z 185.0 (Paraquat)
- Scan: m/z 150-250
- Threshold: 150 counts
- Gain: 2
- Step size: 0.1 amu
- Peak width: 0.1 min
- Time filter: On

	Method Detection Limit	Estimated Reporting Limit
Diquat	0.050 ug/L	0.050 ug/L
Paraquat	0.100 ug/L	0.100 ug/L

Appendix 9. Determination of Selected Herbicides in Water Samples

Appendix 9. Determination of Selected Herbicides in Water Samples

1.0 Scope and Application

1.1 This is a modified EPA Method 615 and describes the sample preparation and quantitative analysis of trace level herbicides in surface, municipal and wastewater using liquid-liquid extraction and high resolution gas chromatography with mass spectrometer-ion trap detector (GC-MS-ITD) The following target analytes can be determined by this method:

1.2 The estimated detection limit for each analyte is listed in Table 1. The actual MDL may differ from those listed, depending upon the nature of interferences in the sample matrix. Validation of the target analytes produced recoveries greater than 65 percent (Appendix I). The mean percent recoveries for each analyte are also included in Table 1.

Table 1. Selected herbicides analyzed by GC/MS/MS, their Minimum Detection Limits (MDL) and Reporting Limits (RL) in water.

Target Analytes	MDL (µg/l)	RL (µg/l)
Oxyfluorfen	0.020	0.050
Propagite	0.200	0.500
Propanil	0.050	0.100
Trifluralin	0.050	0.100

2.0 Summary of Method

2.1 A measured volume of sample (1000 ml) is extracted with methylene chloride (DCM) using a separatory funnel. The DCM extract is dried with sodium sulfate, evaporated using Kuderna-Danish (K-D) and solvent exchanged into petroleum ether. The extract is concentrated with micro-snyder (micro K-D) apparatus to approximately 1 ml and adjusted to 2.0 ml with iso-octane. The extracts are analyzed by gas chromatography using conditions which permit the separation and measurement of the target analytes in the extracts by GC/MS/MS.

2.2 Interferences in analyses may be encountered in very dirty samples and cleanup may be needed to aid in the elimination or reduction of these interferences. Florisil column cleanup or Gel Permeation Chromatography (GPC) procedures will be followed.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may cause GC artifacts and/or elevated baselines, resulting in the misinterpretation of chromatograms. All materials should be demonstrated to be free from interferences under the conditions of the analysis by running method blanks initially and with each sample lot. Specific selection of reagents and purification of solvents by distillation in all-glass systems are required. High-purity distilled-in-glass solvents are commercially available.

An effective way of cleaning laboratory glassware is by rinsing with polar and non-polar solvents before use. The cleaning procedure used must be tested by analyzing procedural blanks prior to analyzing samples.

3.2 Phthalates are common laboratory contaminants that are used widely as plasticizers. Sources of phthalate contamination include plastic lab-ware, plastic tubing, plastic gloves, plastic coated glassware clamps, and have been found as a contaminant in Na_2SO_4.

Polytetrafluoroethylene (PTFE) can be used instead of polypropylene or polyethylene to minimize this potential source of contamination. However, use of PTFE lab-ware will not necessarily preclude all phthalate contamination. Na_2SO_4 can be solvent rinsed to eliminate contaminants.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source. A Florisil or GPC cleanup procedure can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4.0 Apparatus and Laboratory Supplies

4.1 Separatory funnel. 2000-ml, with TFE-fluorocarbon stopcock, ground glass or TEF stopper.

4.2 Automatic shaker designed to fit 2 liter separatory funnels with rpm and timer controls.

4.3 Beakers. Borosilicate glass, 400 mL

4.4 Glass wool. Pyrex - solvent washed prior to use.

4.5 Kuderna-Danish (K-D) Apparatus.

4.5.1 Concentrator tube. 15 mL, graduate (Kontes K0570012-0500, or equivalent). A ground stopper, 19/22 joint, is used to prevent evaporation of extracts.

4.5.2 Evaporation flask. 500 mL (Kontes K-570050-0500, or equivalent), attached to concentrator tube with blue clamp (Kontes K-662750-0012).

4.5.3 Snyder column. Three ball (Kontes K-503000-0121, or equivalent).

4.5.4 Micro-Snyder column. Alltech 9058 or equivalent.

4.5.5 Boiling chips. Hengar granules, high purity amphoteric alundum - extracted with acetone and petroleum ether. Note that boiling chips can be a significant source of contamination if not properly cleaned.

4.6 Water bath. Blue M, 115 V, thermostatically controlled with stainless steel cover to fit K-D apparatus, installed in a fume hood.

4.7 GC vials. GC autosampler vials, borosilicate glass, 2 mL with PTFE-lined screw cap.

4.8 Analytical balance. Capable of weighing 0.1 mg.

4.9 Drying oven.

4.10 Disposable Pasteur Pipettes. 2 mL, rinsed with solvents before use.

4.11 Glass filter funnel. Fluted, 75 mm or larger.

4.12 Graduated cylinder. 1000 ml, 250 mL and 100 mL.

4.13 Culture tubes. 13 x 100 mm with PTFE lined screw cap.

4.14 Analytical systems

4.14.1 Gas chromatograph. Varian 3400, equipped with a Varian Saturn model 2000 Ion Trap Mass Spectrometer, split-splitless injector, LEAP Model CTC A200SE autosampler and a 30 meter capillary column (J&W Scientific).Table 2 lists the operating parameters.

Table 2. Operating parameters for Varian 3400 GC/MS-ITD

Carrier gas:	Helium
Columns:	DB5MS, 30 m x 0.25 mm I.D. x 0.25 µm film thickness
Varian 1078 Inlet:	Isocratic temp @ 240 ºC
Injection Volume:	2 µL
Oven:	Initial temperature: 80 ºC Initial time: 1.200 min Ramp 1: 15.0 deg/min, final temp 175 ºC, hold time 0.50 min Ramp 2: 2.5 deg/min, final temp 220 ºC, hold time 2.00 min Ramp 3: 5.0 deg/min, final temp 260 ºC, hold time 0.00 min

MS-MS Operating Conditions

Trap Temperature:	240 ºC
Manifold Temperature:	80 ºC
Transferline Temperature:	280 ºC
Ionization mode:	EI Auto
Ion preparation:	MS/MS
Scan time:	3µ scan/sec
Emission current;	50 µAmps
Waveform type:	Non-resonant
Filament delay:	5 minute

5.0 Reagents, materials, gases and standards

5.1 Reagent water is defined as water in which an interferent is not observed at method detection limit of each parameter of interest. Deionized (DI) water was used for method validation and as method blank.

5.2 Petroleum ether (PE), acetone, methylene chloride (DCM), diethyl ether, isooctane. Pesticide residue quality or equivalent.

5.3 Sodium sulfate. Anhydrous granular reagent grade, rinsed with PE prior to use.

5.4 Helium. Ultra-pure (99.99999%)

5.5 Stock standards. Individual stock standards (100 µg/ml) are purchased as certified solutions from AccuStandard (New Haven, CT).

6.0 Sample Collection, Preservation, and Storage

6.1 Samples are collected in one liter amber glass bottles and iced or refrigerated at 4 °C from time of collection until extraction.

6.2 All samples must be extracted within 7 days and completely analyzed within 40 days of extraction.

7.0 Sample Extraction

7.1 Remove water samples from refrigerator and allow samples to reach room temperature prior to extraction. Transfer contents to a pre-cleaned 2-liter separatory funnel.

7.2 Add 60 ml of methylene chloride (DCM) to the empty bottle, replace the cap and rinse the bottle. Pour the DCM into the separatory funnel and repeat with another 60 mL aliquot of DCM. Extract the sample by shaking the funnel for 5 minutes on the auto-shaker with periodic venting to release excess pressure. Allow organic layer to separate from the water phase for a minimum of 10 minutes. Collect the methylene chloride extract in a 400 ml beaker.

7.3 Add a second 120 ml volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the beaker.

7.4 Set up and label pre-cleaned K-D flasks with concentrator tubes and attached with a blue clamp on ring stands in the fume hood. Add 0.5 ml iso-octane as "keeper" and a solvent rinsed micro-boiling chip to each K-D concentrator tube. Place a filter funnel containing a plug of pre-cleaned glass wool in the bottom of the funnel and place the funnel in the top of the K-D flask. Add about two inches of solvent rinsed sodium sulfate to the funnel.

7.5 Pour the combined extracts from the beaker through sodium sulfate into the K-D flask. Rinse the beaker with about 10 mL of DCM and add this rinse to the sodium sulfate. Repeat with another 10 mL DCM rinse. Rinse the sodium sulfate with an additional portion of DCM (~10-20 mL).

7.6 Place a Snyder column on the K-D flask, clamp with a green clamp and place the flask on the hot water bath set at 78-82 ^{o}C. Evaporate solvent on the hot water bath. When the apparent volume of solvent in the concentrator tube is 5-10 mL, add 20-30 mL of petroleum ether through the top of the Snyder column. Repeat this procedure when the apparent volume is again at 5-10 mL. When the reflux line falls below the top of the Snyder column, the K-D apparatus should be removed from the hot water bath. Dry the outer KD apparatus with a Kimwipe to prevent condensation water from entering the concentrator tube. Upon cooling, remove the concentrator tube from the K-D apparatus.

7.7 Place a clean micro-Snyder column on the concentrator tube with a blue clamp, add a new micro boiling chip and place in a 400 mL beaker containing water heated to approximately 78 ^{o}C on a hot plate. If the solvent does not begin to boil, remove the tube from the bath immediately, allow it to cool slightly, add a new micro boiling stone to prevent it from bumping and place it back in the bath.

7.8 When the solvent has been evaporated to 0.5-1 mL remove the tube from the bath and allow it to cool in a test tube rack. Dry the outer KD apparatus with a Kimwipe to prevent condensation water from entering the concentrator tube. Remove the micro-Snyder column and add iso-octane to the concentrator tube to reach a final volume of 2.0 mL. Mix the tube contents by

tapping the bottom of the tube causing a vortex which will rinse the sides of the tube. A Vortex Genie mixer may be used for this step.

7.9 Transfer the solution from the concentrator tube to a culture tube and cap with a Teflon™ faced cap. Place extracts in a refrigerator for storage until analysis or cleanup, if necessary.

7.10 When ready for analysis, transfer extract to labeled GC vials and cap.

8.0 Cleanup Procedure

8.1 Cleanup of dirty samples may be necessary due to interferences in the analysis of baseline or co-elution with target analytes of the sample extract. Follow the in-house SOP for Florisil® column or GPC method, as needed.

9.0 Analytical Procedure

9.1 The final extract will be analyzed on a Varian 3400 gas chromatograph equipped with a Saturn model 2000 Ion Trap Mass Spectrometer. See analytical method for details.

Appendix 10. Methanol Material Safety Data Sheet (MSDS)

Material Safety Data Sheet

Methanol

ACC# 14280

Section 1 - Chemical Product and Company Identification

MSDS Name: Methanol
Catalog Numbers: AC167830025, AC167835000, AC176840010, AC176840025, AC176845000, AC177150010, AC177150025, AC177150250, AC268280010, AC268280025, AC325740025, AC326630010, AC326630025, AC326950010, AC326951000, AC326952500, AC327900010, AC364390010, AC364391000, AC413770040, AC413775000, AC423950010, AC423950040, AC423950200, AC423955000, AC610090040, AC610200040, AC610400010, AC61040019, AC61040019, AC61040050, AC610401000, AC61040115, AC61040115, AC61040200, AC61040200, AC610550190, AC610550500, AC610551150, AC610552000, AC610750190, AC610750500, AC610751150, AC610752000, AC610981000, AC611070040, S75162, S75163, S75959, S75965, S75965A, S75965HPLC, S75965SPEC, S93301, S93301A, S93302, S93302A, A408-1, A408-4, A408-4LC, A408SK-4, A411-20, A411-4, A412-1, A412-20, A412-200, A412-200LC, A412-4, A412-4LC, A412-500, A412-500LC, A412CU1300, A412FB115, A412FB19, A412FB200, A412FB50, A412J500, A412P-4, A412P-4LC, A412POP19, A412POPB200, A412RB115, A412RB200, A412RB50, A412RS115, A412RS19, A412RS200, A412RS28, A412RS50, A412SK-4, A412SS-115, A413-20, A413-200, A413-4, A413-500, A433F-1GAL, A433P-4, A433P1GAL, A433RS50, A433S-20, A433S-200, A433S-4, A434-20, A450-4, A452-1, A452-212, A452-4, A452-4LC, A452J1, A452N119, A452N219, A452POP200, A452POP28, A452POP50, A452RS-115, A452RS-19, A452RS-200, A452RS-28, A452RS-50, A452SK-1, A452SK-4, A452SS-19, A452SS-200, A452SS-50, A452SS28, A452SS50, A453-1, A453-1LC, A453-500, A453J1, A454-1, A454-1LC, A454-4, A454-4LC, A454J1, A454POP50, A454RS-115, A454RS-200, A454RS-28, A454SS-28, A454SS-50, A454SS200, A455-1, A455RS19, A457-4, A4574LC, A935-4, A935RB200, A947-4, A947-4LC, A947POP200, A947RS-115, A947RS-200, A947RS-28, A947SS-115, A947SS-200, A947SS-28, A947SS-50, BP1105-1, BP1105-4, BP1105SS19, BP1105SS28, BP2618100, HC400 1GAL, METH, NC9105104, NC9134255, NC9173853, NC9283877, NC9397156, NC9541632, NC9942270, NC9964975, PS03496, SC95-1, SW2-1, TIA9474, TIA947P200L
Synonyms: Carbinol; Methyl alcohol; Methyl hydroxide; Monohydroxymethane; Wood alcohol; Wood naptha; Wood spirits; Columbian spirits; Methanol.
Company Identification:

Fisher Scientific
1 Reagent Lane
Fair Lawn, NJ 07410

For information, call: 201-796-7100
Emergency Number: 201-796-7100
For CHEMTREC assistance, call: 800-424-9300
For International CHEMTREC assistance, call: 703-527-3887

Section 2 - Composition, Information on Ingredients

CAS#	Chemical Name	Percent	EINECS/ELINCS
67-56-1	Methanol	> 99	200-659-6

Section 3 - Hazards Identification

EMERGENCY OVERVIEW

Appearance: clear, colorless liquid. Flash Point: 11 deg C.

Danger! Poison! **Flammable liquid and vapor.** May be fatal or cause blindness if swallowed. Causes respiratory tract irritation. Harmful if swallowed, inhaled, or absorbed through the skin. Vapor harmful. Causes eye and skin irritation. May cause central nervous system depression. Cannot be made non-poisonous.

Target Organs: Eyes, nervous system, optic nerve.

Potential Health Effects

Eye: Methanol is a mild to moderate eye irritant. Inhalation, ingestion or skin absorption of methanol can cause significant disturbances in vision, including blindness.

Skin: Causes moderate skin irritation. Harmful if absorbed through the skin. Prolonged and/or repeated contact may cause defatting of the skin and dermatitis. Methanol can be absorbed through the skin, producing systemic effects that include visual disturbances.

Ingestion: Harmful if swallowed. May be fatal or cause blindness if swallowed. Aspiration hazard. May cause systemic toxicity with acidosis. May cause central nervous system depression, characterized by excitement, followed by headache, dizziness, drowsiness, and nausea. Advanced stages may cause collapse, unconsciousness, coma and possible death due to respiratory failure.

Inhalation: Methanol is toxic and can very readily form extremely high vapor concentrations at room temperature. Inhalation is the most common route of occupational exposure. At first, methanol causes CNS depression with nausea, headache, vomiting, dizziness and incoordination. A time period with no obvious symptoms follows (typically 8-24 hrs). This latent period is followed by metabolic acidosis and severe visual effects which may include reduced reactivity and/or increased sensitivity to light, blurred, double and/or snowy vision, and blindness. Depending on the severity of exposure and the promptness of treatment, survivors may recover completely or may have permanent blindness, vision disturbances and/or nervous system effects.

Chronic: Prolonged or repeated skin contact may cause dermatitis. Chronic exposure may cause effects similar to those of acute exposure. Methanol is only very slowly eliminated from the body. Because of this slow elimination, methanol should be regarded as a cumulative poison. Though a single exposure may cause no effect, daily exposures may result in the accumulation of a harmful amount. Methanol has produced fetotoxicity in rats and teratogenicity in mice exposed by inhalation to high concentrations that did not produce significant maternal toxicity.

Section 4 - First Aid Measures

Eyes: In case of contact, immediately flush eyes with plenty of water for a t least 15 minutes. Get medical aid.
Skin: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical aid immediately. Wash clothing before reuse.
Ingestion: Potential for aspiration if swallowed. Get medical aid immediately. Do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person.
Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid.
Notes to Physician: Effects may be delayed.
Antidote: Ethanol may inhibit methanol metabolism.

Section 5 - Fire Fighting Measures

General Information: Containers can build up pressure if exposed to heat and/or fire. As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. During a fire, irritating and highly toxic gases may be generated by thermal decomposition or combustion. Use water spray to keep fire-exposed containers cool. Water may be ineffective. Material is lighter than water and a fire may be spread by the use of water. Flammable liquid and vapor. Vapors are heavier than air and may travel to a source of ignition and flash back. Vapors can spread along the ground and collect in low or confined areas.
Extinguishing Media: For small fires, use dry chemical, carbon dioxide, water spray or alcohol-resistant foam. Water may be ineffective. For large fires, use water spray, fog or alcohol-resistant foam. Do NOT use straight streams of water.
Flash Point: 11 deg C (51.80 deg F)
Autoignition Temperature: 464 deg C (867.20 deg F)
Explosion Limits, Lower:6.0 vol %
Upper: 36.00 vol %
NFPA Rating: (estimated) Health: 1; Flammability: 3; Instability: 0

Section 6 - Accidental Release Measures

General Information: Use proper personal protective equipment as indicated in Section 8.
Spills/Leaks: Absorb spill with inert material (e.g. vermiculite, sand or earth), then place in suitable container. Use water spray to disperse the gas/vapor. Remove all sources of ignition. Provide ventilation. A vapor suppressing foam may be used to reduce vapors. Water spray may reduce vapor but may not prevent ignition in closed spaces.

Section 7 - Handling and Storage

Handling: Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Ground and bond containers when transferring material. Avoid contact with eyes, skin, and clothing. Empty containers retain product residue, (liquid and/or vapor), and can be dangerous. Keep container tightly closed. Do not ingest or inhale. Do not pressurize, cut, weld, braze, solder, drill, grind, or expose empty containers to heat, sparks or open flames. Use only with adequate ventilation. Keep away from heat, sparks and flame. Avoid use in confined spaces. Avoid breathing vapor or mist.
Storage: Keep away from heat, sparks, and flame. Keep away from sources of ignition. Store in a cool, dry, well-ventilated area away from incompatible substances. Flammables-area. Keep containers tightly closed.

Section 8 - Exposure Controls, Personal Protection

Engineering Controls: Use explosion-proof ventilation equipment. Facilities storing or utilizing this material should be equipped with an eyewash facility and a safety shower. Use adequate general or local exhaust ventilation to keep airborne concentrations below the permissible exposure limits.
Exposure Limits

Chemical Name	ACGIH	NIOSH	OSHA - Final PELs
Methanol	200 ppm TWA; 250 ppm STEL; Skin - potential significant contribution to overall exposure by the cutaneous r oute	200 ppm TWA; 260 mg/m3 TWA 6000 ppm IDLH	200 ppm TWA; 260 mg/m3 TWA

OSHA Vacated PELs: Methanol: 200 ppm TWA; 260 mg/m3 TWA
Personal Protective Equipment
Eyes: Wear chemical splash goggles.
Skin: Wear appropriate protective gloves to prevent skin exposure.
Clothing: Wear appropriate protective clothing to prevent skin exposure.
Respirators: A respiratory protection program that meets OSHA's 29 CFR 1910.134 and ANSI Z88.2 requirements or European Standard EN 149 must be followed whenever workplace conditions warrant respirator use.

Section 9 - Physical and Chemical Properties

Physical State: Liquid
Appearance: clear, colorless
Odor: alcohol-like - weak odor
pH: Not available.
Vapor Pressure: 127 mm Hg @ 25 deg C

Vapor Density: 1.11 (Air=1)
Evaporation Rate:5.2 (Ether=1)
Viscosity: 0.55 cP 20 deg C
Boiling Point: 64.7 deg C @ 760 mm Hg
Freezing/Melting Point:-98 deg C
Decomposition Temperature: Not available.
Solubility: miscible
Specific Gravity/Density:.7910 g/cm3 @ 20°C
Molecular Formula:CH4O
Molecular Weight:32.04

Section 10 - Stability and Reactivity

Chemical Stability: Stable under normal temperatures and pressures.
Conditions to Avoid: High temperatures, ignition sources, confined spaces.
Incompatibilities with Other Materials: Strong oxidizing agents, strong acids, powdered aluminum, powdered magnesium.
Hazardous Decomposition Products: Carbon monoxide, irritating and toxic fumes and gases, carbon dioxide, formaldehyde.
Hazardous Polymerization: Will not occur.

Section 11 - Toxicological Information

RTECS#:
CAS# 67-56-1: PC1400000
LD50/LC50:
CAS# 67-56-1:
Draize test, rabbit, eye: 40 mg Moderate;
Draize test, rabbit, eye: 100 mg/24H Moderate;
Draize test, rabbit, skin: 20 mg/24H Moderate;
Inhalation, rabbit: LC50 = 81000 mg/m3/14H;
Inhalation, rat: LC50 = 64000 ppm/4H;
Oral, mouse: LD50 = 7300 mg/kg;
Oral, rabbit: LD50 = 14200 mg/kg;
Oral, rat: LD50 = 5600 mg/kg;
Skin, rabbit: LD50 = 15800 mg/kg;
Human LDLo Oral: 143 mg/kg. LDLo Oral: 428 mg/kg. TCLo Inhalation; 300 ppm caused visual field changes & headache. y LDLo Skin: 393 mg/kg. nol is significantly less toxic to most experimental animals than humans, because most animal species metabolize methanol differently. Non-primate species do not ordinarily show symptoms of metabolic acidosis or the visual effects which have been observed in primates and humans.
Carcinogenicity:
CAS# 67-56-1: Not listed by ACGIH, IARC, NTP, or CA Prop 65.

Epidemiology: No data available.
Teratogenicity: There is no human information available. Methanol is considered to be a potential developmental hazard based on animal data. In animal experiments, methanol has caused fetotoxic or teratogenic effects without maternal toxicity.
Reproductive Effects: See actual entry in RTECS for complete information.

Mutagenicity: See actual entry in RTECS for complete information.
Neurotoxicity: ACGIH cites neuropathy, vision and CNS under TLV basis.
Other Studies:

Section 12 - Ecological Information

Ecotoxicity: Fish: Fathead Minnow: 29.4 g/L; 96 Hr; LC50 (unspecified)Fish: Goldfish: 250 ppm; 11 Hr; resulted in deathFish: Rainbow trout: 8000 mg/L; 48 Hr; LC50 (unspecified)Fish: Rainbow trout: LC50 = 13-68 mg/L; 96 Hr.; 12 degrees CFish: Fathead Minnow: LC50 = 29400 mg/L; 96 Hr.; 25 degrees C, pH 7.63Fish: Rainbow trout: LC50 = 8000 mg/L; 48 Hr.; UnspecifiedBacteria: Phytobacterium phosphoreum: EC50 = 51,000-320,000 mg/L; 30 minutes; Microtox test No data available.
Environmental: Dangerous to aquatic life in high concentrations. Aquatic toxicity rating: TLm 96>1000 ppm. May be dangerous if it enters water intakes. Methyl alcohol is expected to biodegrade in soil and water very rapidly. This product will show high soil mobility and will be degraded from the ambient atmosphere by the reaction with photochemically produced hyroxyl radicals with an estimated half-life of 17.8 days. Bioconcentration factor for fish (golden ide) < 10. Based on a log Kow of -0.77, the BCF value for methanol can be estimated to be 0.2.
Physical: No information available.
Other: No information available.

Section 13 - Disposal Considerations

Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. US EPA guidelines for the classification determination are listed in 40 CFR Parts 261.3. Additionally, waste generators must consult state and local hazardous waste regulations to ensure complete and accurate classification.
RCRA P-Series: None listed.
RCRA U-Series:
CAS# 67-56-1: waste number U154 (Ignitable waste).

Section 14 - Transport Information

	US DOT	Canada TDG
Shipping Name:	METHANOL	METHANOL
Hazard Class:	3	3(6.1)
UN Number:	UN1230	UN1230
Packing Group:	II	II
Additional Info:		FLASHPOINT 11 C

Section 15 - Regulatory Information

US FEDERAL

TSCA

CAS# 67-56-1 is listed on the TSCA inventory.

Health & Safety Reporting List

None of the chemicals are on the Health & Safety Reporting List.

Chemical Test Rules

None of the chemicals in this product are under a Chemical Test Rule.

Section 12b

None of the chemicals are listed under TSCA Section 12b.

TSCA Significant New Use Rule

None of the chemicals in this material have a SNUR under TSCA.

CERCLA Hazardous Substances and corresponding RQs

CAS# 67-56-1: 5000 lb final RQ; 2270 kg final RQ

SARA Section 302 Extremely Hazardous Substances

None of the chemicals in this product have a TPQ.

SARA Codes

CAS # 67-56-1: acute, flammable.

Section 313

This material contains Methanol (CAS# 67-56-1, > 99%),which is subject to the reporting requirements of Section 313 of SARA Title III and 40 CFR Part 373.

Clean Air Act:

CAS# 67-56-1 is listed as a hazardous air pollutant (HAP).

This material does not contain any Class 1 Ozone depletors.

This material does not contain any Class 2 Ozone depletors.

Clean Water Act:

None of the chemicals in this product are listed as Hazardous Substances under the CWA.

None of the chemicals in this product are listed as Priority Pollutants under the CWA.

None of the chemicals in this product are listed as Toxic Pollutants under the CWA.

OSHA:

None of the chemicals in this product are considered highly hazardous by OSHA.

STATE

CAS# 67-56-1 can be found on the following state right to know lists: California, New Jersey, Pennsylvania, Minnesota, Massachusetts.

California Prop 65

California No Significant Risk Level: None of the chemicals in this product are listed.

European / International Regulations

European Labeling in Accordance with EC Directives

Hazard Symbols:

T F

Risk Phrases:

R 11 Highly flammable.

R 23/24/25 Toxic by inhalation, in contact with skin and if

swallowed.
R 39/23/24/25 Toxic : danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.

Safety Phrases:

S 16 Keep away from sources of ignition - No smoking.
S 36/37 Wear suitable protective clothing and gloves.
S 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S 7 Keep container tightly closed.

WGK (Water Danger/Protection)

CAS# 67-56-1: 1

Canada - DSL/NDSL

CAS# 67-56-1 is listed on Canada's DSL List.

Canada - WHMIS

This product has a WHMIS classification of B2, D1B, D2B.

Canadian Ingredient Disclosure List

CAS# 67-56-1 is listed on the Canadian Ingredient Disclosure List.

MSDS Creation Date: 7/21/1999

Revision #12 Date: 11/03/2004