

QUALITY ASSURANCE PROJECT PLAN
IMPERIAL VALLEY PESTICIDES TMDL ASSESSMENT
STUDIES

SWRCB No. 05-278-250-0

January 2007

Prepared for
State Water Resources Control Board
Regional Water Resources Control Board- Region 7

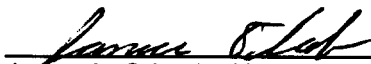
Prepared by
U.S. Geological Survey California Water Science Center




Quality Assurance Project Plan
IMPERIAL VALLEY PESTICIDES TMDL ASSESSMENT STUDIES

APPROVALS:

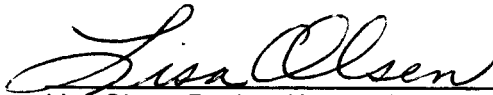
U.S. Geological Survey


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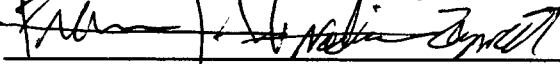

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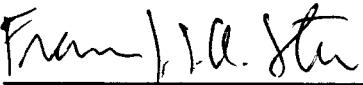

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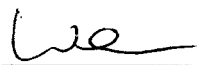
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1. PROJECT MANAGEMENT

1.1 INTRODUCTION

The California Regional Water Quality Control Board (Regional Board), Colorado River Basin Region develops and implements water pollution control programs to protect the health of human and biological communities. There is a direct relationship between water quality and ecosystem health. Effective ecosystem protection and management is dependent upon knowing: (1) how water quality variables affect an ecosystem, and (2) how chemicals and materials are transported in the water column. Interactions of chemicals and materials within an ecosystem are influenced by environmental changes. These changes alter the physiological conditions of biota or the physicochemical characteristics of the system.

Water Quality Standards (WQS) adopted for the Colorado River Basin Region are contained in the region's Water Quality Control Plan. WQS for the Alamo and New Rivers are comprised of beneficial uses and the water quality objectives (numerical or narrative) designed to protect the most sensitive beneficial use. The most sensitive beneficial uses for the Alamo and New Rivers are: warm freshwater habitat (WARM); wildlife habitat (WILD); preservation of rare, threatened, and endangered species (RARE); contact and non-contact recreation (REC I and REC II), and freshwater replenishment (FRSH). The New and Alamo Rivers are included in the CWA 303(d) list due to impairments in water quality objectives and beneficial uses.

Regional Board staff have developed a standard agreement (SWRCB No. 05-278-250-0) with the U.S. Geological Survey (USGS) to conduct a detailed study to assess the occurrence, transport, and fate of historical and current-use pesticides in the Alamo and New Rivers. The USGS will conduct six sampling events beginning in September 2006 and ending in April 2007. The USGS will analyze water and suspended sediment samples using pesticide analysis techniques developed during previous studies in the Salton Sea region. The USGS will provide quarterly progress reports to the Regional Board describing activities, task accomplishments, milestones achieved, and problems encountered. Following completion of the April 2007 sampling event and analysis, the USGS will provide a draft final report describing the work performed and analysis results.

Field and laboratory work will be carried out utilizing Quality Assurance Project Plan (QAPP) protocols outlined in this document. The QAPP encompasses activities associated with the sampling and analysis of pesticides in the Alamo and New Rivers. This QAPP is subject to approval by the USGS, Regional Board staff. The QAPP follows the format established by the USEPA in *Requirements for Quality Assurance Project Plans, EPA QA/R-5, 2001*, and complies with SWRCB quality assurance/quality compliance (QA/QC) procedures. Any revisions by the USGS or Regional Board must be mutually agreed upon.

The USGS project QA/QC officer and project director are responsible for ensuring that QAPP protocols are followed. The project QA/QC officer will be independent from the units generating data for the project. The QA/QC officer may, upon mutual concurrence, modify this QAPP to achieve project objectives.

1.1 PROJECT/TASK ORGANIZATION

➤ U.S. GEOLOGICAL SURVEY STAFF

USGS Project Director

James L. Orlando, Hydrologist, (916) 278-3271. Coordinates and conducts sampling and ensures that sampling procedures conform to project plan guidelines. Processes data, maintains database, and disseminates data in conjunction with USGS Project Director.

USGS Administrative Representative

Kathryn Kuivila, (916) 278-3054. Ensures Quality Assurance Project Plan (QAPP) is implemented and meets project objectives. Reports to the Regional Board Contract Manager regarding project status per the work plan.

USGS Project Quality Assurance/Quality Control Officer

Lisa Olsen (916) 278-3084. Coordinates activities with Regional Board. Reviews and approves QAPP with SWRCB Quality Assurance/Quality Control Officer. Conducts project activities in accordance with the QAPP and work plan. Processes data, maintains database, and disseminates data in conjunction with USGS Project Director.

Field and Analytical Staff

Kelly Smalling, Chemist (916) 278-3052. Shares responsibility with James Orlando for conducting sampling events and ensuring that sampling procedures conform to project plan guidelines. Conducts analyses and ensures that the laboratory adheres to QA/QC procedures. Assisted by Jason Cooper, Student Assistant

Michelle Hladik, Ph.D. Chemist, (916) 278-3183. Conducts analyses and ensures that the laboratory adheres to QA/QC procedures. Assisted by Jason Cooper, Student Assistant

➤ REGIONAL BOARD STAFF

Regional Board Contract Manager

Nadim Zeywar, PhD, Senior Environmental Scientist, (760) 776-8932. Ensures Quality Assurance Project Plan (QAPP) is implemented and meets project objectives. Reports to the SWRCB regarding project status per the work plan.

Regional Board Contract Contact

Francisco Costa, PhD, Environmental Scientist, (760) 776-8937. Coordinates and manages contracts and budget. Documents problems resulting from inadequate implementation of QA/QC procedures. Reports problems to USGS Project Manager for corrective action. Reviews reports and ensures plans are implemented according to schedule.

SWRCB Quality Assurance/Quality Control Officer

Bill Ray, Staff Environmental Scientist, (916) 341-5583. Coordinates activities with USGS. Reviews and approves QAPP. Conducts project activities in accordance with the QAPP and work plan. Processes data, maintains database, and disseminates data in conjunction with Project Director.

1.2 BACKGROUND/PROBLEM DEFINITION

The Colorado River Basin Region is a desert region covering over 20,000 square miles in the southeastern corner of the State. One of the dominant land uses is agriculture, with irrigated farmlands in the Coachella, Imperial, and Palo Verde Valleys. These valleys are some of the most productive agricultural areas in the State. Most agricultural irrigation drainage water from this area proceeds from fields into drainage canals, which ultimately lead to the Salton Sea. The rivers and the Salton Sea provide habitat for aquatic and avian species, and are used for water contact recreation such as boating, swimming, and fishing. Non-point source pollution due to agricultural runoff is the most severe water quality problem in the region and is the target of present and future water pollution control efforts.

The study area (Fig.1) includes the Alamo and New Rivers south from the Salton Sea to the U.S./Mexico border within Imperial County. The Salton Sea is a terminal quasi-marine lake fed largely by agricultural irrigation drainage water that enters through the Alamo and New Rivers. The Alamo and New Rivers also receive small amounts of treated sewage from Imperial Valley municipalities, and the New River receives additional untreated and under-treated sewage from Mexicali, Mexico (Setmire, 1994). Still, the predominant source of water in these rivers is agricultural irrigation drainage water.

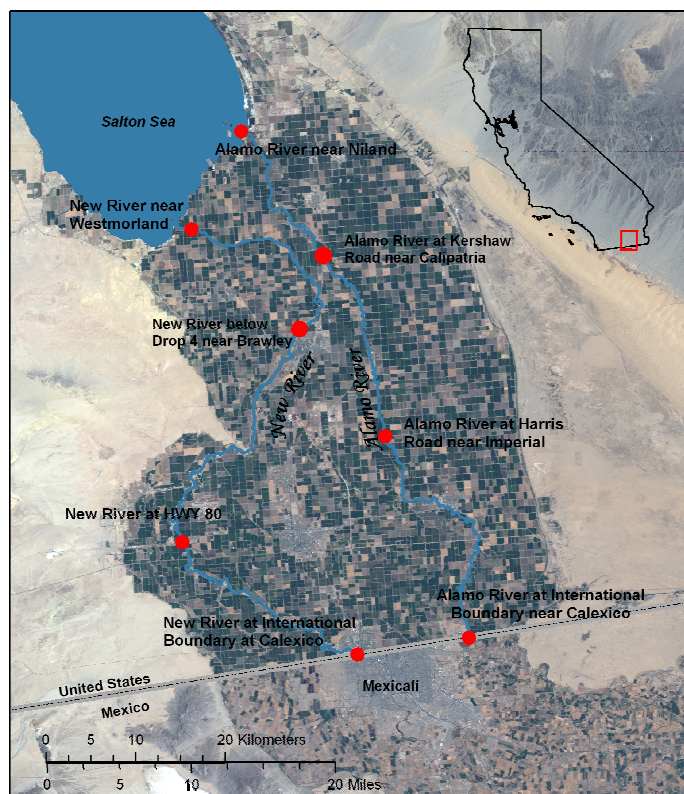


Fig.1. Sampling locations for the Alamo and New Rivers.

Depths of the Alamo and New Rivers at their outlets to the Salton Sea are a little over one meter, and suspended sediment concentrations are a few hundred milligrams per liter. USGS gaging stations and bridges exist at the outlets of both rivers. Daily mean flows on the Alamo and New Rivers, as measured near their outlets to the Salton Sea, range from 468 to 1,127 cfs and from 511 to 749 cfs, respectively (U.S. Geological Survey, 2005).

Deposition from high loads of suspended sediment delivered by the rivers has resulted in the formation of broad regions of shallow water (deltas) at the mouth of the rivers. These shallow areas are ecologically important as they harbor large numbers of fish and birds, including endangered or threatened species. These shallow areas also include, or are adjacent to, federal and state wildlife refuges.

Over 3 million pounds of pesticide active ingredients (excluding sulfur), were applied to approximately 60 different crops in the region in 2004 (California Department of Pesticide Regulation, 2005). Pesticide applications follow a bimodal pattern with peaks in October and March. During 2004, over 130 individual pesticides were applied in the region.

Several USGS studies since the late 1960s have identified the presence of pesticides associated with agriculture in the Salton Sea area. Recent results, as well as ongoing plans by regulatory agencies to develop Total Maximum Daily Loads (TMDLs) for this area, have indicated the need for a more complete understanding of the occurrence, transport, and fate of pesticides.

The earliest USGS pesticide study in the Salton Basin involved DDT analysis in the Alamo and New Rivers for 12 months in 1969-70 (Irwin, 1971). High concentrations were found in the river water itself because DDT was still being used in the U.S. and Mexico. DDT was no longer detected in the water in 1986 (Setmire and others, 1990), 14 years after DDT was banned in the U.S. and 3 years after its ban in Mexico. However, DDT's metabolite, DDE, was present in bottom materials from both rivers, and the upstream to downstream trend in its concentration matched that of aqueous DDT concentrations observed nearly 20 years earlier (Schroeder, 1996). This was taken as strong evidence that DDT, or its metabolites persisted in local soils and today continues to be transported to drains and rivers in tail water.

Several USGS studies during the last 30 years have documented the widespread presence of many commonly used pesticides. Bimonthly monitoring for a period of one year in 1977-78 showed that concentrations for many "current-use" pesticides in Imperial Valley drains and rivers matched their seasonal pattern of application, with maxima occurring in the late winter/early spring and again in the early fall (Eccles, 1979). Concentrations in USGS samples collected in March/April 1992 (R. Schroeder, USGS, written commun. 1992, and in 1995-96 (draft pending publication by the International Boundary and Water Commission) are consistent with this pattern.

The Eccles study found that neither current-use nor historical (DDT and its metabolites) pesticides were present in subsurface drainage water. Irrigation water applied to soil takes about 5 years to be discharged by subsurface drains (Michel and Schroeder, 1994), thus indicating removal of pesticides by adsorption on soils and/or by biodegradation. Time is an important factor in the substantial removal of pesticides from water in areas that are far removed from the Salton Sea shore (unpublished data from R. Schroeder, USGS, written communication. 1992). Residence time (lake volume divided by annual recharge) is approximately 6 years and water circulation time is about several months in the Salton Sea, thus permitting partial or complete removal in portions of the interior lake by adsorption onto particles, chemical and biological degradation, and photo-oxidation.

Monthly monitoring on the Alamo River in 1994-95 by the University of California, Davis (de Vlaming and others, 2000) confirmed the same temporal pattern and implicated 5 commonly used pesticides--2 carbamates (carbaryl and carbofuran) and 3 organophosphates

(malathion, diazinon, and chlorpyrifos)--as the cause of high mortality in laboratory toxicity tests using *Ceriodaphnia dubia*. A later collaborative study with the USGS from 1996-1998 included chemical analysis of a larger suite of pesticides in which elevated concentrations of 9 different pesticides were detected at concentrations greater than 10 µg/L in surface water collected on the southern shore near where the Alamo and New Rivers and numerous agricultural drains enter the Salton Sea (Crepeau, and others, 2002). Further toxicity testing by the University of California, Davis in 2001-2002 again found high toxicity to *C. dubia* and *N. mercedis* in the Alamo River as well as toxicity to these same test organisms in water samples from the New River (de Vlaming and others, 2004).

Two recent studies conducted by the USGS in 2001-02 and in 2003 found elevated concentrations of current-use pesticides and the organochlorine degradates DDD and DDE in water, suspended sediment, and bed sediment, in the Alamo and New Rivers, and Salton Sea (Leblanc, and others 2004a,b). These studies found generally higher concentrations of pesticides in the Alamo River than in the New River. Pesticide concentrations were also generally higher in suspended sediment samples than in bed sediment samples.

The mechanism for pesticide transport in water is thought to be through adsorption to silt particles originating from agricultural field runoff. Silt, and consequently pesticides, is conveyed from the field by tail water, which settles in drains, rivers, and the Salton Sea. The objective of this study is to determine the occurrence, transport, and fate of historical and current-use pesticides in the Alamo and New Rivers. A major component will be to determine pesticides distribution between water and suspended sediment.

1.3 PROJECT/TASK DESCRIPTION

Regional Board staff developed a standard agreement (SWRCB No. 05-278-250-0) with the U.S. Geological Survey (USGS) to conduct a detailed study to assess the occurrence, transport, and fate of historical and current-use pesticides in the Alamo and New Rivers. In total eight sites will be sampled, four sites each along the Alamo and New Rivers. Both water and suspended sediment will be collected for analysis. The furthest upstream sites will be at the U.S./Mexico border, while the furthest downstream sites will be at the outlet of each river into the Salton Sea. Two additional sites will be sampled on each river proximate (and downstream of) inputs from major agricultural drains. Six sampling events are scheduled: in September 2006, October 2006, November 2006, February 2007, March 2007, and April 2007. During the September, November, February, and April sampling events only the outlets of each river to the Salton Sea will be sampled. In October 2006 and March 2007 all eight sites will be sampled.

Fifty-nine current-use pesticides will be analyzed in water, and 59 current-use pesticides and 26 legacy pesticides will be analyzed in suspended sediments (Table 1). Pesticides will be analyzed as described in Leblanc and others (2004a) and Smalling and others (2005). Special mention is made of pyrethroids, a class of insecticides that is increasing in use, very toxic to fish, and likely to bind to sediments.

Suspended sediment samples will be collected by pumping water via a peristaltic pump into pre-cleaned 20-L stainless steel cans. The volume of water collected will range from about 300 to 900 L at each site, with the largest volumes collected at the international boundary sites, where suspended sediment concentrations are expected to be lowest. The suspended material will be isolated by pumping the water sample through a Westfalia continuous-flow centrifuge as described in Bergamaschi et al. (1999) and Horowitz et al. (1989). Water samples for the analysis of dissolved pesticides will be collected from the centrifuge effluent, and will be a composite of the entire sample. Methods for the extraction and analysis of surface water samples are modified from Crepeau et al. (2000) and involve the use of Oasis HLB solid phase extraction cartridges. Methods for extraction of suspended sediments will be based upon methods described in LeBlanc et al. (2004a, b), and Smalling et al. (2005) with modifications to optimize sample preparation.

The Project Director and/or the Quality Assurance Officer will assess data from each sampling event. The assessment will be based on results of quality control activities such as: (a) analysis of quality-control samples, and (b) quality-control procedures followed during sample collection, storage, and analysis.

1.4 DATA QUALITY OBJECTIVES

The data obtained for this project will assess the occurrence, transport, and fate of pesticides in the Alamo and New Rivers. Regional Board staff will use the data for basin planning purposes (e.g., TMDLs, adequacy of water quality standards to protect beneficial uses). Strict adherence to collection techniques, preservation requirements, holding times, and analytical methodology will ensure high quality, and these data quality objectives are listed in tables 1, 3 and 4.

1.5 SPECIAL TRAINING/CERTIFICATION

Field and laboratory personnel are trained in basic first-aid, defensive driving, hazard communication, laboratory safety, and in sampling from cableways.

1.7 DOCUMENTATION AND RECORDS

USGS field staff will keep field notes, sample-collection forms, copies of chain of custody forms, and quality control sample records for each sampling event. Sample-collection forms and field notes will be kept in a bound field notebook. Information recorded will include: sample identification codes, collection points, time of collection, names of individuals collecting samples, methods used for sample collection, and field observations. Quality-control records will document the preparation and use of quality-control samples, and equipment calibration. Chain of custody forms will have the sample identification codes, collection times and locations, and signatures of all individuals in custody of the samples.

The laboratory will provide information for samples analyzed including: names of individuals analyzing samples, time and date of analysis, and any deviations from standard operating procedures. Analytical laboratory staff will transfer data (including metadata) from laboratory forms to a computerized database. The database will be utilized for data validation, assessment, and report writing. Database maintenance and documentation/records storage will be the responsibility of the Project Director, who will provide quarterly and final reports to the Regional Board.

2. DATA GENERATION AND ACQUISITION

2.1 SAMPLING DESIGN

USGS staff will collect samples from eight monitoring sites: four on both the Alamo and New Rivers. Water and suspended sediment will be collected at each site and the samples analyzed for pesticides utilizing the methodologies or modified methodologies of Crepeau et al. (2000), LeBlanc et al. 2004a, and Smalling et al (2005). Six sampling events are scheduled: in September 2006, October 2006, November 2006, February 2007, March 2007, and April 2007. These are the times of expected maximum pesticide concentrations. The USGS Project Director and/or Regional Board QA/QC Officer will evaluate the data generated from each sampling event to determine if QAPP changes are necessary. The following paragraphs discuss the rationale for selection of samples, constituents, and sampling sites.

2.2 SAMPLING SITES

Four sites each will be sampled along the Alamo and New Rivers for water and suspended sediment. The furthest upstream sites will be at the U.S./Mexico border, while the furthest downstream sites will be at the outlet of each river into the Salton Sea. Two additional sites will be sampled on each river proximate (and downstream of) inputs from major agricultural drains. With the exception of the Alamo River international boundary site, all samples will be collected from bridges or cableway. Six sites will be identical to sites sampled during a recent USGS study (Fig. 1) (Leblanc and others, 2004b) Two other sites (one on each river) will be selected prior to the initial sampling and will be located at bridge crossings, downstream of major agricultural drain inputs. Six sampling events are scheduled: in September 2006, October 2006, November 2006, February 2007, March 2007, and April 2007. During the September, November, February, and April sampling events only the outlets of each river to the Salton Sea will be sampled. In October 2006 and March 2007 all eight sites will be sampled. At all sites, cross-stream heterogeneity will be characterized by measuring dissolved oxygen, pH, turbidity, specific conductance, and temperature at several evenly-spaced points along the width of the river and at several depths. In addition, streamflow measurements will be made during each sampling event at ungaged sites, following established USGS methods (Buchanan and Somers, 1969).

2.3 FIELD MEASUREMENTS AND SAMPLE-COLLECTION METHODS

Field measurements will be made of dissolved oxygen, pH, turbidity, specific conductance, and temperature at all sites immediately prior to sampling. Measurements will be made using a Hydrolab Surveyor 4 hand-held multi-parameter meter (HACH Environmental, Loveland, CO, USA), calibrated prior to each use.

Water and suspended samples will be collected and processed using the methods described in Leblanc and others, (2004a). Briefly, samples will be collected from multiple points and depths along a stream transect using a high-volume peristaltic pump fitted with Teflon tubing. The collected water will be pumped into pre-cleaned 20-L stainless steel soda kegs. The volume collected will range from about 300 to 900 L, depending on suspended-sediment concentrations. The objective is to process a sufficient volume of water to obtain at least 20 grams of suspended sediment.

The water sample will be pumped through a Westphalia continuous-flow centrifuge operating at 9,500g at the rate of 2 L/min to segregate the liquid and solid phases and concentrate the suspended sediments ($> 0.3 \mu\text{m}$) into a slurry. The centrifuge flow rate is based on a study of particle trapping efficiency by Horowitz and others (1989) who found that 2 L/min using the Westphalia centrifuge yields in the optimum particle trapping efficiency. The water

exiting the centrifuge represents the liquid phase and will be analyzed for dissolved pesticides. The sediment slurry remaining in the centrifuge will be further dewatered at the laboratory using a high-speed refrigerated centrifuge operating at 15,000 revolutions per minute. The segregated water and sediment samples will be stored at 4 °C and -20 °C, respectively prior to analysis.

Sample identification codes, field observations, and any deviations from standard operating procedures will be recorded in the field notebook immediately following sample collection. Sample holding times prescribed by the Surface Water Ambient Monitoring Program (SWAMP) will be implemented. Preservation containers, preservation techniques, and holding times for constituents analyzed are listed in Table 1.

Table 1. Required Containers, Preservation Techniques, and Holding Times

Constituent	Container	Preservation Technique	Holding Time
Water	Amber Glass Bottles	Cool Below 4 °C	7 days ¹
Suspended Sediments	Stainless Steel or Glass Bottles	Cool Below -20 °C	12 months ²

¹ Provided the water is filtered within the initial 24 hours of sampling

² Stored frozen

2.4 SAMPLING CONSTITUENTS

USGS staff will collect and analyze water for 59 current-use pesticides and suspended sediment, samples for 59 current-use and 26 legacy organochlorine pesticides. These pesticides were chosen based upon current or historical use in the Salton Basin, occurrence in environmental samples, and probable occurrence based upon physical characteristics of the pesticides (generally a log K_{oc} > 3.0). The pesticides that will be analyzed are listed in Table 2.

Table 2. List of compounds to be analyzed, organized by chemical class

Compound	Chemical Class	Compound	Chemical Class
Ethalfuralin	Anilines	Chlorpyrifos	Organophosphates
Pendamethalin	Anilines	Diazinon	Organophosphates
Trifluralin	Anilines	Disulfoton	Organophosphates
Carbaryl	Carbamates	Fenamiphos	Organophosphates
Carbofuran	Carbamates	Malathion	Organophosphates
Alachlor	Chloacetanilides	Methidathion	Organophosphates
Metolachlor	Chloacetanilides	Methylparathion	Organophosphates
Azoxystrobin	Fungicides	Phosmet	Organophosphates
Chlorothalonil	Fungicides	Allethrin	Pyrethroids
Cyproconazole	Fungicides	Bifenthrin	Pyrethroids
Metconazole	Fungicides	Cyfluthrin	Pyrethroids
Myclobutanil	Fungicides	Cypermethrin	Pyrethroids
Propiconazole	Fungicides	Deltamethrin	Pyrethroids
Pyraclostrobin	Fungicides	Esfevalerate	Pyrethroids
Tebuconazole	Fungicides	Fenpropathrin	Pyrethroids
Tetraconazole	Fungicides	Lambda-Cyhalothrin	Pyrethroids
Trifloxystrobin	Fungicides	Permethrin	Pyrethroids
α -chlordane	Organochlorines	Sumithrin	Pyrethroids
α -HCH	Organochlorines	Tau-Fluvalinate	Pyrethroids
Aldrin	Organochlorines	Tetramethrin	Pyrethroids
β -HCH	Organochlorines	Butylate	Thiocarbamates
<i>cis</i> -nonachlor	Organochlorines	Cycloate	Thiocarbamates
δ -HCH	Organochlorines	EPTC	Thiocarbamates
Dieldrin	Organochlorines	Molinate	Thiocarbamates
Endosulfan I	Organochlorines	Pebulate	Thiocarbamates
Endosulfan II	Organochlorines	Thiobencarb	Thiocarbamates
Endosulfan sulfate	Organochlorines	Atrazine	Triazines/Triazones
Endrin	Organochlorines	Hexazinone	Triazines/Triazones
Endrin aldehyde	Organochlorines	Prometryn	Triazines/Triazones
γ -chlordane	Organochlorines	Simazine	Triazines/Triazones
γ -HCH	Organochlorines	Dacthal (DCPA)	Misc.
Heptachlor	Organochlorines	Dichloroaniline	Misc.
Heptachlor epoxide	Organochlorines	Fipronil	Misc.
Hexachlorobenzene	Organochlorines	Fipronil desulfinyl	Misc.
Isodrin	Organochlorines	Fipronil sulfide	Misc.
Methoxychlor	Organochlorines	Fipronil sulfone	Misc.
Oxychlordane	Organochlorines	Iprodione	Misc.
<i>p,p'</i> DDD	Organochlorines	Methoprene	Misc.
<i>p,p'</i> DDE	Organochlorines	Napropamide	Misc.
<i>p,p'</i> DDT	Organochlorines	Oxuflofen	Misc.
Pentachloronitrobenzene	Organochlorines	Piperonyl butoxide	Misc.
Pentachloroanisole	Organochlorines	Propanil	Misc.
<i>trans</i> -nonachlor	Organochlorines		

2.5 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Each sample container will be labeled with a unique sample identification code that includes the date, location, and time the sample was collected. Samples will be stored in a cooler immediately after collection. The chests will contain sufficient ice to maintain sample temperature below 4°C until relinquished to analytical laboratory personnel. See Section 5.5 for additional details on packing and shipping samples.

All samples will be delivered with appropriate chain-of-custody forms. Any violation in holding time, sample handling, custody requirements, etc., will be reported to the Project Director and the project QA/QC Officers, and recorded in the quality control records for consideration during data validation (see Section 4.1).

2.6 ANALYTICAL METHODS AND REQUIREMENTS

Water samples will be analyzed for pesticides by extracting one liter of sample water onto Oasis HLB solid-phase extraction (SPE) cartridges. Prior to extraction, all water samples will be spiked with ^{13}C -atrazine, and ^{13}C -diazinon as recovery surrogates. The SPE cartridges will be dried with carbon dioxide, eluted with 12 mL of ethyl acetate, and deuterated internal standards will be added to the eluant. All sample extracts will be analyzed by gas chromatography-mass spectrometry (GC-MS). Additional details are given in Crepeau and others, 2000.

Sediment samples will be extracted based on modifications to methods described by LeBlanc et al. (2004) and Smalling et al. (2005). Briefly, wet sediments (~50% moisture) will be extracted two times using a MSP 1000 (CEM Corporation, Mathews, North Carolina) microwave-assisted solvent extraction (MASE) with dichloromethane (DCM) and acetone (Jayaraman et al. 2001). The extracts will be dried over sodium sulfate and reduced to 1 mL using a Turbovap II (Zymark Corporation, Hopkinton, Massachusetts). The sediment matrix will be removed by passing the sample extract through two stacked solid-phase extraction (SPE) cartridges containing 500-mg nonporous, graphitized carbon (Restek Corporation, Bellefonte, VA) and 500-mg alumina (Varian Inc., Palo Alto, California). The cartridges will then be washed in tandem with 10 mL of DCM prior to the addition of the sample extract. Compounds of interest are then eluted off both SPE cartridges with 10 mL of DCM and collected as fraction 1 (F1). The carbon SPE is removed and the alumina SPE is eluted with 10 mL of ethyl acetate and DCM (50:50 v/v) and collected as fraction 2 (F2). The two fractions are kept separate and evaporated under a gentle stream of purified nitrogen gas (N-evap, Organomation Associates, Berlin, Massachusetts) to 0.5 mL and exchanged to ethyl acetate. Sulfur, will be removed using a gel-permeation/high-pressure liquid chromatography system (GPC/HPLC) from the first fraction only. The two fractions are then reduced to 0.2 mL under a gentle stream of N_2 and the deuterated PAH internal standard mixture added.

Surface-water and suspended-sediment sample extracts (1 μL injection volume) will be analyzed using either a Varian Saturn 2000 gas chromatograph/mass spectrometer (GC/MS) with ion-trap detection or an Agilent 6890 gas chromatograph with a micro-electron capture detector (GC- μECD). Analyte separation on the GC/MS is achieved using a 30 m x 0.25 mm i.d. x 0.25 μm film thickness HP-5MS capillary column (Agilent Technology, Folsom, CA), with Helium as the carrier gas. The temperature of the injector is set at 275 °C, and the trap, manifold and transfer line temperatures are set at 220, 80, and 280 °C respectively. The GC oven program will be as follows: 80 °C (hold 0.5 min), ramp to 120 °C at 10 °C/min; , ramp to 200 °C at 3 °C/min (hold 5 min), ramp to 219 °C at 3 °C/min (hold 5 min), ramp to 300 °C at 10 °C/min (hold 10 min). Complete details of the analytical method are described in Crepeau et al. (2000) and LeBlanc et al. (2004). Analyte separation on the GC/ μECD is achieved using a 30 m x 0.25 mm i.d. x 0.25 μm film thickness DB-XLB fused-silica capillary column (Agilent Technology, Folsom, CA), with helium as the carrier gas. The split/splitless injector and detector temperatures are 250 and 330

°C, respectively. The initial GC oven temperature of 75 °C (0.5 min. hold) is followed by an increase to 300 °C at 10 °C/min.

2.7 QUALITY QUALITY-CONTROL REQUIREMENTS

A number of quality-control checks will be implemented to assess whether data quality requirements are being met. All quality-control checks meet or exceed SWAMP requirements.

Table 3 compares the project QA/QC plan with SWAMP QC requirements for organic constituents (pesticides) in water.

QC Sample Type	SWAMP Requirements	Project QA/QC	Acceptance Criteria ¹
External/Internal Calibration	Follow manufacturer's or procedures in specific analytical protocols. A minimum 3 point calibration at each set up, major disruption, and when routine calibration check exceeds specific control limits.	8 point calibration curve ranging from 0.025 to 5 ng/uL at each instrument set up, major disruption, and when routine calibration check exceeds specific control limits.	Linear regression, $r > 0.995$.
Calibration Verification	After initial calibration or recalibration. Every 10 samples.	After initial calibration or recalibration. Every 6 samples.	%Recovery = 80 -115%
Laboratory Blanks	One method blank per 20 samples or one per batch, whichever is more frequent. At least one bottle blank per batch. One reagent blank prior to use of a new batch of reagent and whenever method blank exceeds control limits.	One method blank per 10 samples or one per batch, whichever is more frequent. Laboratory blanks should comprise 10 % of all samples per sampling event.	Blanks <MDL for target analyte.
CRM (Reference Material)	Method validation: As many as required to assess accuracy and precision of method before routine analysis of samples. Routine accuracy assessment: one (preferably blind) per 20 samples or one batch.	National Water Quality Laboratory Schedule 2003/2033 (1 µg/mL) spiked into 1 L sample water. Routine accuracy assessment every 10 samples	Measured value <95% confidence intervals, if certified. Otherwise, %Recovery = 50-150%.

Matrix Spikes	One per 20 samples or one per batch, whichever is more frequent.	One per 10 samples or one per batch, whichever is more frequent. Matrix spikes will comprise 10 % of all samples per sampling event	%Recovery = 80-120% or Control Limits based on 3x the standard deviation of laboratory's actual method recoveries.
Matrix Spike Replicate	One duplicate per 20 samples or one per batch, whichever is more frequent.	One duplicate per 20 samples per sampling event	RPD <25% for duplicates.
Surrogate Spikes	In every calibration standard, sample, and blank analyzed for organics by GC or isotope dilution GC-MS; added to samples prior to extraction.	Isotopically labeled compounds added to every sample and blank analyzed for organics by GC-MS; added to samples prior to extraction.	% Recovery = 80-120%
Field Blanks	Random performance evaluation during field audit; field blanks <MDL for analyte of interest. If acceptable performance, no field blanks required until next field audit. If non-acceptable, 5% field blanks must be conducted during the year until next field audit.	Field blanks <MDL for analytes of interest. Field blanks should comprise 10 % of all samples per sampling event	Blanks <MDL for target analyte.
Field Replicate	5% annual rate (5% of total number of field samples per analytical procedure per year, rounded up to nearest whole number).	One per 10 samples or one per batch, whichever is more frequent. Replicates should comprise 10 % of all samples per sampling event.	RPD <25% for duplicates.

¹ Meets both SWAMP and project QA/QC plan criteria

Table 4 compares the project QA/QC plan with SWAMP QC requirements for organic constituents (pesticides) in sediment.

QC Sample Type	SWAMP Requirements	Project QA/QC Plan	Acceptance Criteria ¹
Internal Calibration	Follow manufacturer's or procedures in specific analytical protocols. A min., 3 point calibration at each set up, major disruption, and when routine calibration check exceeds specific control limits.	8 point calibration curve ranging from 0.025 to 5 ng/uL at each instrument set up, major disruption, and when routine calibration check exceeds specific control limits.	Linear regression, $r > 0.995$.
Calibration Verification	After initial calibration or recalibration. Every 10 samples.	After initial calibration or recalibration. Every 6 samples.	%R = 85-115%.
Laboratory Blanks	One method blank per 20 samples or one per batch, whichever is more frequent. At least one bottle blank per batch. One reagent blank prior to use of a new batch of reagent and whenever method blank exceeds control limits.	One method blank per 10 samples or one per batch, whichever is more frequent. Laboratory blanks should comprise 10 % of all samples per sampling event.	Concentration of any analyte <MDL as determined by program manager.
CRM (Reference Material)	Method validation: As many as required to assess accuracy and precision of method before routine analysis of samples. Routine accuracy assessment: one (preferably blind) per 20 samples or one batch.	Standard reference material (SRM 1941b) Organics in marine sediment. Routine accuracy assessment analyzed every 20 samples.	Measured value 70-130% of the 95% confidence intervals, if certified. Otherwise, % Recovery = 50-150%.
Matrix Spikes	One per 20 samples or one per batch, whichever is more frequent.	One per 10 samples or one per batch, whichever is more frequent. Matrix spikes will comprise 10 % of all samples per sampling event	%Recovery = 50-150% or Control Limits based on 3x the standard deviation of laboratory's actual method recoveries.
Matrix Spike Replicate	One duplicate per 20 samples or one per batch, whichever is more frequent.	One duplicate per 20 samples per sampling event	RPD <25% for duplicates.

Surrogate Spike	In every calibration standard, sample, and blank analyzed for organics by GC or isotope dilution GC-MS; added to samples prior to extraction.	Isotopically labeled compounds added to every sample and blank analyzed for organics by GC-MS; added to samples prior to extraction.	Determined by program manager.
Field Blanks	One travel blank and one field blank is required per every 20 (or less) field samples collected for volatile organic analytes (VOC's, MTBE, BTEX) in sediment. No travel, field, or equipment blanks are required for other (non-volatile, semi-volatile) organic compound samples in sediment or tissue.	Not applicable	Blanks<MDL.
Field Replicate	One field duplicate sample per 20 samples or one per batch, whichever is more frequent.	One per 10 samples or one per batch, whichever is more frequent. Replicates should comprise 10 % of all samples per sampling event.	RPD <25% for duplicates.

¹ Meets both SWAMP and project QA/QC plan criteria.

2.8 METHOD VALIDATION, INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

Proper maintenance procedures for instruments and equipment will be followed and documented. To ensure that equipment is operating properly and that data quality is high, the USGS laboratory staff will employ quality assurance, quality control, and corrective measures. These measures will include the following:

Reference standards will be analyzed periodically, using the same procedures as are used for the environmental samples during GC-MS analyses. A standard should be analyzed after every sixth sample injection to verify that the analyte calibration curves are within operational specifications. If the measured concentrations of the standards differ by more than 25 % from expected concentrations, the corresponding environmental samples should be re-analyzed after the source of the problem is determined and corrected.

Method validation will consist of the determination of method detection limits (MDLs) as well as the evaluation of spiked samples (matrix spikes) and surrogate recoveries described briefly in section 2.7. Method detection limits and mean accuracy (recovery) will be assessed by spiking Alamo and New River water and suspended-sediment samples with known amounts of each compound and analyzing as a sample. The analytical method for surface water and suspended sediment will be validated by spiking seven replicates of a natural sample with a mixture of pesticides to determine method detection limits (MDLs) (U.S. Environmental Protection Agency, 1992). Analytes identified at concentrations less than the MDL will be reported as estimated values. Matrix spiked percent recoveries of each compound will be calculated to determine the effectiveness of the methods used to measure each compound. Each sample will be spiked with a surrogate prior to extraction to monitor the efficiency of each extraction. The compounds in the surrogate mixture include ¹³C-labeled atrazine, diazinon, trifluralin,

chlorpyrifos, *p,p'*-DDE and permethrin (*cis/trans* mixture) (Cambridge Isotope Laboratories Inc., Andover, Massachusetts). Surrogate recoveries are required to be within the control limits (± 2 standard deviations from the mean) for data to be included in the final data set.

2.9 INSTRUMENT CALIBRATION AND FREQUENCY

Initial calibration curves will be generated on each instrument (GC/MS and GC/ μ ECD) using standard solutions containing all of the target pesticides before sample analysis begins. Computer software will be used to generate linear regression equations for pesticide response over the concentration range of the calibration curve (0.025-5.0 ng/ μ L for GC/MS and 1-100 pg/ μ L for GC/ μ ECD). Calibration curves will be accepted when the correlation coefficient is greater than 0.99. Calibration will be checked frequently by analyzing standards throughout the sample analysis, but at the very least once every 8 hours during the sample analysis period. Pesticide quantification in the environmental samples will continue as long as the calibration curves are verified to be acceptable.

Location, temperature, dissolved oxygen (DO), pH, turbidity, and electrical conductance measurements will be taken in the field using a GPS unit, and a multiparameter meter. Accuracy of the GPS unit will be confirmed by checking against readings obtained at established gaging stations. Standards will be used to test the accuracy of the multiparameter meter for all parameters not less than once per sampling event.

2.10 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES/CONSUMABLES

Supplies and consumables will be purchased through local vendors, scientific supply houses, or USGS centralized warehouses. They will be deemed acceptable unless inspection reveals lack of compliance with expected criteria. For example, any solvents that are used will be expected to be of pesticide grade or better as indicated on the label. Containers, such as cleaned and oven-baked pesticide bottles, supplied through USGS centralized warehouses are periodically checked to confirm absence of pesticide residues.

2.11 DATA ACQUISITION REQUIREMENTS (NON-DIRECT METHODS)

The USGS has collected data for the Alamo and New Rivers in previous years. Relevant data collected from these sampling events will be utilized for policy-making, pending data validation and quality assessment. Criteria for accepting previously collected data include representativeness of similar conditions, documented bias, methods of data evaluation, applicability to this project, and data summarization. USGS staff will interpret data and provide conclusions.

2.12 DATA MANAGEMENT

Data will be entered into the USGS National Water Information System (NWIS) database. Data will also be stored locally in an Access database and in Excel spreadsheets. Backup (multiple copies) of data will be made routinely by personnel in the USGS Water Science Center in Sacramento. In addition, all 8 sampling sites are, or will be, established as formal stations in the USGS NWIS database and will include metadata such as location, elevation, and types of data collected.

3. ASSESSMENT AND OVERSIGHT

3.1 ASSESSMENT AND RESPONSE ACTIONS

Surveillance of records and overall project status will be conducted by the Project Director. Surveillance will be conducted following each sampling event, and after laboratory results have been received.

The Project Director will perform a technical systems audit. During this audit, the Project Director will examine field activities and record-keeping procedures to assess their conformance to the QAPP. This audit will take place after each sampling trip. Any non-conformance with the QAPP will be corrected and documented as described in Section 4.2. The laboratory's QA procedures and QC results for this project also will be reviewed. Laboratory performance will be assessed using quality-control samples, namely field blanks, replicate samples and matrix-spike samples.

Prior to preparing a final report, an audit of data quality will be performed to assess data management, and if necessary correct any errors in the project database. Statistical tools will be utilized to determine: (a) if the data satisfy the assumptions of the data-quality objectives and sampling design, and (b) whether the total error in the data is tolerable.

3.2 REPORTS TO MANAGEMENT

Upon completion of the project, the USGS Project Director or another party delegated by the director will prepare a final project report. The report will include a summary of the activities performed, the data collected, and an assessment of data quality.

3.3 PHOTOGRAPHIC DOCUMENTATION OF THE SAMPLING SITES

The sampling sites and surroundings will be photographed for documentation and included in the field log. Each photo will include site identification, date and time taken, and photo orientation.

4. DATA VALIDATION AND USABILITY

USGS and Regional Board staff will validate data to ensure QA guidelines were followed. The QA performed will ensure that data transfer is free of errors, and that results are reasonable relative to data previously collected/analyzed.

4.1 VERIFICATION AND VALIDATION METHODS

The USGS Project Director will review field notes and field data for each sampling event to verify that the sampling design was followed (i.e., spatial distribution of sampling locations, sample collection protocol). Departures from the sampling design will be considered in the design of each subsequent sampling event. Deviations may be necessary to better characterize the system, or to accommodate unforeseen field conditions. Significant departures in sampling design (e.g., changes in sampling sites or sample collection procedures) will be noted in the project database, audit of data quality, and final report. The Project Director and QA/QC Officer will evaluate: (a) the effects of all deviations (if any) on overall data completeness, and (b) data usability for supporting conclusions. Changes in sampling design must adhere to data quality objectives as outlined in this document, and original and modified methods should produce directly comparable results as supported in accepted literature.

Field records, technical systems audits, and project surveillance will be used to verify proper sample collection and equipment decontamination procedures. Analytical results for equipment blanks also may verify proper equipment decontamination. All of this information will be considered in the final audit of data quality. Departures from sample collection and equipment decontamination procedures that would be considered unacceptable include the use of contaminated sampling bottles, lack of critical sample collection information, cross-contamination or incorrect identification of samples.

Potential departures from the sample handling and custody procedures will be determined by reviewing chain of custody forms and laboratory analysis forms. For data to be considered valid the chain of custody forms for all samples must be in the possession of the Project Manager and strict adherence to holding times and temperatures must be followed.

Quality-control records will be reviewed to verify proper calibration of field equipment, and will be documented in the audit of data quality. If errors in calibration values exceed error tolerances, the measurements obtained prior to that calibration, but after the previous calibration, will be labeled “suspect”, and investigated to determine their validity for this study.

Validation of laboratory data will be performed in the audit of data quality by assessing the results of QC sample analyses. Laboratory data will be validated for precision, accuracy, and completeness according to the criteria discussed below.

4.2 RECONCILIATION WITH USER REQUIREMENTS

The Project Director will be responsible for oversight of sampling and quality-assurance procedures in the field and for ensuring that all data are entered in the USGS NWIS database and local Access database. The interpretation needs are comparisons to historical data and replicate analyses, distribution of constituent concentrations in various phases (dissolved and suspended material), constituent spatial distribution, and evaluation of QA/QC data.

The Regional Board QA/QC Officer will be responsible for validating and approving all data used in this study. The final project report will discuss relevant information obtained from the audit of data quality, such as the quality, validity completeness, and limitations of data. The report

also will discuss the results of statistical analyses performed on the data set as part of the data quality assessment.

4.3 DATA STATISTICAL ANALYSIS

The analytical data generated by this project is the product of a research, as opposed to a monitoring, study and hence does not lend itself to complex statistical interpretation. This study does not require complex statistical analysis because of the relatively small number of samples that will be collected at each site. The only use of statistics will be 1) in ascertaining the adequacy of the instrument blanks and spike recoveries, and 2) in comparing duplicate (replicate) analyses for selected field samples. "Replicate" data are generated whenever splits from a sample or blank are processed separately, and whenever the isolate from processing is injected into the instrument more than once. Criteria, in terms of percent difference for acceptance of results based on these replicate analyses are discussed in Section 2.8.

5. HEALTH AND SAFETY PLAN

5.1 CONTAMINATION CONTAINMENT

The contaminated area consists of the entire waterways of the aforementioned rivers, their banks, and the area within 2 feet of the banks. Decontamination zones will be designated at least 10 feet from the riverbank. The decontamination zone will be used for personnel decontamination and will include wash water, soap, paper towels, and trash bags. All contaminated solid waste material will be placed in trash bags for proper disposal. Only biodegradable antibacterial soap will be used. Wash water runoff will be contained and disposed of in the surface water downstream of the sampling point. The clean zone will be designated at least 20 feet from the riverbank.

5.2 PERSONAL PROTECTIVE EQUIPMENT (PPE)

General concerns at the sampling sites include: exposure to toxicants in the water being sampled, being struck by an automobile when taking samples near roads or bridges, tripping and falling, drowning, venomous snakes, insect bites, sunburn, excessive heat exposure, and biohazard exposure. A good practice is to have at least three experienced field samplers at each sampling event

- To reduce the risk of exposure to toxicants in the water being sampled, all samplers will wear a face shield or goggles, two pairs of nitrile gloves, tyvek suit or isolation gown, and boot covers. **The Contaminated Zone must not be entered without the aforementioned PPE.**
- To reduce the risk from automobile traffic, traffic cones will be placed at 30-foot intervals to form a “safety corridor” at least five feet in width, between the traffic and sampling crew. The safety corridor will be constructed at roads, bridges, or where traffic is reasonably expected to be present. Warning flags will be placed along the roadside at least 200 feet from the safety corridor in the direction of oncoming traffic and a vehicle with emergency flashers will be parked at the end of the corridor. The parked vehicle and safety cones must be clearly visible to on-coming traffic from a distance of at least 120 feet. Samplers will wear orange vests when sampling near roads.
- To reduce the risk from tripping and falling, field personnel will inspect areas for ladders, steps, farm structures (e.g., ponds, water tanks, and reservoirs), slopes, holes, construction hazards, and other hazards.
- To reduce the risk of drowning, field personnel will use personal flotation devices (PFD) when collecting samples. PFDs include the standard jacket type and the suspender type.
- To reduce the risk of venomous snake bites, high boots will be worn. First aid procedures for venomous snake bites include: keeping the patient calm, removing tight fitting clothing, shoes, etc., removing jewelry, keeping the bite below the level of the heart, and transporting the victim to the nearest medical facility. If the snake has been killed, it will be brought to the medical facility with the patient.
- To reduce the risk of insect bites, insect repellents will be used.

- To reduce the risk of sunburn and excessive heat exposure, field personnel will wear sunscreen, and the vehicle will contain ample cold drinking water. If personnel begin to experience symptoms of heat exhaustion, such as cramps or dizziness, he or she will immediately be removed to a shaded area or air conditioned vehicle and given plenty of cool liquids. If these symptoms persist the effected worker will be transported to the nearest hospital (See Section 5.4).
- To reduce the risk of biohazard exposure, the following actions will be implemented for biohazards: don protective clothing, spray the spill area with disinfectant, cover the spill with an absorbent blanket marked with a biohazard sign, dispose of blanket in biohazard waste bag (after all liquid is absorbed), remove protective clothing and clean hands with sanitizing gel.

5.3 PERSONNEL DECONTAMINATION PROCEDURES

The clean zone must not be entered with contaminated PPE. All team members exiting contaminated zones must immediately proceed to the decontamination zone. The following decontamination procedures will be implemented before proceeding to the clean zone:

1. Remove boot covers and place them in a plastic bag.
2. Wash outer rubber gloves with antibacterial soap prior to removal of other PPE. Place outer gloves in the storage bin labeled "Decontamination PPE No. 1".
3. Carefully remove tyvek suit and place in the storage bin labeled PPE No. 2," or a plastic bag (avoid skin contact to exterior of suit).
4. Remove face shield or goggles and place in a plastic bag.
5. Remove latex gloves carefully to avoid contact with bare skin and dispose of in a trash bag. Thoroughly wash hands with antibacterial soap or Betadiene antiseptic and rinse thoroughly with more clean water.
6. Dispose of wash water into the river or ground.

All items contacting dirty gloves could be contaminated (pens, pencils, rinse water bottles, probes, etc.). Avoid touching these items with bare skin.

5.4 DECONTAMINATION PROCEDURES

Decontamination of field equipment (e.g., the pump) and sampling containers (e.g., the large stainless steel canisters), will proceed as follows: rinse successively with tap water, acetone, methanol, and deionized water. Any "mud" that adheres to the centrifuge bowl will be removed with brushes and spatulas prior to washing with deionized water and solvents. Laboratory equipment will be cleaned and decontaminated, and investigative-derived waste will be disposed of following appropriate procedures established within the California Water Science Center.

5.5 SAMPLE SHIPPING AND HANDLING

Cooler chests containing samples packed in ice will be shipped for overnight delivery by FEDEX to the USGS laboratory in Sacramento. Shipments will be made within 2 or 3 days of sample collection, depending on load and excluding weekends. Solid-phase material will be frozen as soon as received at the laboratory pending further processing. Laboratory

personnel will use appropriate handling practices when working with solid-phase material, and appropriate PPE (gloves, goggles or face shield and laboratory aprons) will be worn at all times. See section 2.5 for additional information on sample handling and shipment.

5.6 EMERGENCY NUMBERS AND FACILITIES

All sampling personnel will have access to a cellular phone to call 911 in case of an emergency. Hospitals closest to the sampling locations are listed below:

1. El Centro Regional Medical Center. Imperial and Ross Ave., El Centro, CA. Phone: (760) 339-7100
2. Pioneers Memorial Hospital. 207 West Legion, Brawley, CA. Phone: (760) 351-3333.

In an emergency, sampling personnel also should contact Ronald G. Fay, USGS Health and Safety Officer, San Diego, CA. Phone: (858)637-6846

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