California Department of Food and Agriculture
Environmental Monitoring and Pest Management
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Protocol for a Spatial and Temporal Survey of Pesticides in the San Joaquin River

I. Introduction

In 1988 personnel from the Central Valley Regional Water Quality Control Board (CVRWQCB) began testing water quality in the San Joaquin River (SJR) watershed using bioassays. The purpose of these tests was to characterize water quality in both the SJR and its major tributaries in order to identify sources of toxicity (Connor 1988). A subsequent series of memorandums from the CVRWQCB indicated that bioassays conducted on water from Orestimba Creek, SJR at Crows Landing and Laird Park, Lateral Drain #5, and occasionally SJR at Maze Rd and Mossdale, created substantial mortality in *Ceriodaphnia* sp. (Foe 1989, Foe 1990). The specific cause of toxicity was not determined but was attributed to pesticides rather than to heavy metal contamination or other water quality parameters (personal communication, Bob Gilliom, U.S. Geological Survey, and Chris Foe, CVRWQCB). Only water samples that were highly toxic in bioassay tests were analyzed for pesticides. Pesticides detected in those analyses include, but are not necessarily limited to: diazinon, ethyl parathion, carbaryl, dimethoate and carbofuran. Many of these exceeded EPA water-quality criteria and/or LC50 concentrations, when such values were available. Additional information on the ammonia content of water samples and pesticide content of water samples where toxicity did not occur was not reported.

In addition to the work conducted by the CVRWQCB, personnel at the U.S. Geological Survey (USGS) have monitored organochlorine pesticide residues

in sediment of the SJR (Gilliom and Clifton 1990). Although the discussion centered on DDT, DDD, DDE, and dieldrin (compounds which have been cancelled), it provided useful information on areas where soil erosion problems exist. Other compounds detected in sediment samples include chlordane, endosulfan, mirex and toxaphene. Of these, only endosulfan is actively registered. Study findings indicate that sediment from tributaries along the westside of the SJR contain the highest residues of pesticides. These tributaries include the Newman wasteway, and Orestimba, Ingram and Hospital Creeks (Figure 1). Orestimba Creek is also a location from which toxicity was found in bioassay tests.

Data concerning the spatial and temporal distribution of pesticides in water of the SJR is not abundant. The temporal pattern of certain pesticides has been routinely monitored by the USGS at one site on the SJR. This site, near Vernalis (Figure 1), is sampled monthly as part of the National Stream Quality Accounting Network. Pesticides detected in river water at Vernalis (water year 1989) include: cyanazine, diazinon, ethion, lindane, methyl and ethyl parathion, and metolachlor (Anderson et al., 1990). Information about pesticide residues at sites other than Vernalis has been collected once a year during 1985-7 (Shelton and Miller, 1988). However, seasonal water sampling at a number of sites over the course of one or two years has not been attempted.

Due to the reported biotoxicity of SJR water and the need for more information concerning spatial and temporal patterns of pesticide residues in the river, personnel from the Environmental Hazards Assessment Program (EHAP) will be conducting a three part study. Part one, described here, will be a survey to determine the spatial and temporal distribution of pesticides in SJR water. Study results from this segment will then be used to identify regions and seasons of high contamination. Once those are determined, the pesticides of concern will be identified and future research conducted on the mechanisms of off-target movement. Once these mechanisms are understood, control measures can be implemented. In addition, water samples will be tested for ammonia content in the field to try and determine if *Ceriodaphnia* sp. mortality is related to this contaminant.

Part two, to be described in a separate protocol, will consist of collecting about 40 water samples along with the CVRWQCB during their proposed bioassay testing to: 1. provide an interlab comparison of pesticide results for their upcoming study, and 2. to provide information on the pesticide content of samples where toxicity does not occur in bioassay tests. Sample collection will be spread out over an 18-month period. This protocol will be developed shortly after the CVRWQCB completes the details of their sampling plan in November, 1990.

Part three will be a modeling effort to determine if it is feasible to predict pesticide content of SJR water from known source inputs. No additional sampling will be required for this portion: the details of which will be described in a separate protocol. Data collected in Part one will be coordinated with requirements for modelling needs.

II. Objectives

1. To determine the spatial and temporal distribution of organophosphorous (OP) and carbamate pesticides in water from the San Joaquin River using a Lagrangian sampling scheme. This information will be used to identify pesticides of concern, and the seasons and regions of importance in terms of river contamination.

2. To analyze the ammonia content of water samples to address the possibility that *Ceriodaphnia* sp. mortality might be related to this contaminant.

III. Personnel

This study will be conducted by EHAP personnel as follows:

Project Leader:	Lisa Ross
Field Coordinator:	Roger Sava
Senior Review:	Bruce Johnson

Laboratory Liason:	Randy Segawa
Chemist:	Enseco-Cal Laboratories
Agency & Public Contact:	Madeline Ames

ALL QUESTIONS CONCERNING THIS STUDY SHOULD BE DIRECTED TO MADELINE AMES AT: (916) 324-8916.

IV. Study Plan

Below its headwaters in the Sierra Nevada Mountains, the SJR extends about 213 km from Friant Dam to Stevenson where flows are intermittent (Gilliom and Clifton 1990). Between Stevenson and Vernalis (about 97 km), flows are perennial and the major tributaries entering the SJR are the Merced, Tuolumne, and Stanislaus Rivers, in addition to irrigation-return flows (Figure 1). The USGS and the California Department of Water Resources currently maintain 5 gaging stations along this section of the SJR. Those stations are located near Stevenson, Newman, Patterson, Maze Road, and Vernalis (Figure 1). In addition, the USGS is operating gaging stations on Orestimba Creek and the Tuolumne River. Water sampling will be conducted at or near these gaging stations to take advantage of information currently collected there (e.g. discharge, temperature and specific conductivity). The upper most sampling point on the SJR (Stevenson) was selected because water flow is intermittent above this point and toxicity has rarely been seen upstream. Sites on the Tuolumne and Stanislaus Rivers were selected because these are the main drainage pathways for agricultural land east of the SJR in Stanislaus County. Additional sites will be located on Salt and Mud Sloughs, Los Banos, Del Puerto, Ingram and Hospital Creeks, and TID Lateral No. 5 plus Newman Wasteway (Figure 1). Other sites (e.g. Laird Park and Merced River) will be substituted for those listed above when flow rates dictate the need to do so. In addition, sampling sites on all tributaries will be located as close as possible to the main stem of the SJR.

The sampling strategy will follow a Lagrangian design where a "parcel" of water is sampled as it moves downstream. Water sampling will therefore be

coordinated with flow rates. It has been estimated that water takes an average of 2.86 days to travel from Stevenson to Vernalis (Clifton and Gilliom 1989), therefore sites listed above will be sampled during the course of a 2 to 3 day period each time samples are to be collected.

Water sampling will be conducted during 3, 8-week "seasons". Using the list of compounds that can be quantified in the OP and carbamate screens plus the 1988 pesticide use data, it appears that Jan-Feb, March-April-May, and July-Aug-Sept are the 3 "seasons" of highest use. During each season, water samples will be collected 3 times at 16 locations (see above). The site at Patterson (or Laird Park) will be sampled twice a week to provide information on the temporal variation of pesticide concentrations during each "season". In addition, this information will be used to trigger "seasonal" sampling at the 16 locations. Should the turnaround time for pesticide analyses be too long, the start-up date for sampling will also be coordinated with peak pesticide usage (as indicated by county agricultural use reports) and mortality information from bioassays conducted by the CVRWQCB.

In addition to water sampling, other parameters including: total suspended sediment and organic carbon content, discharge, dissolved oxygen, light penetration, water temperature, electrical conductivity, and pH will be collected at each site. General climatic data and river geometry (e.g. width and depth) will also be recorded during sampling.

This research effort will be coordinated with studies being conducted by the USGS and the CVRWQCB. In executing this study design, sampling efforts will be aided by USGS staff as specified under research contract.

Total Number of Samples for chemical analysis (Including Quality Control Samples):

Water: 16 sites x 3 seasons x 4 samples per season	= 192
Quality Control Samples (10%) - water only	= 19
Total (including QC)	= 211

V. Sampling Methods

Four, one-liter water samples will be collected at each of the 16 sampling sites (Figure 1). Two of these samples will be used for chemical analysis, one for an organophosphorous screen, the other for a carbamate screen. The third sample will be used to analyze total suspended sediment and organic carbon, while the fourth will serve as a back-up sample.

Water samples will be collected with a USGS, D-77 sampler modified for pesticide sampling. Sampling will be conducted using the equal-width increment, depth integration method (Guy and Norman 1970), with a series of 10 to 30 verticals per cross section of river or tributary, where feasible. Sampling will be performed either from a bridge or by wading, when applicable. Water will not be filtered and therefore pesticide contents will reflect the mass contained in a total water sample. Water will be placed in one-liter amber glass jars and sealed with aluminum-lined caps. Samples will be acidified with 3 N HCl to a pH of 3 to 4 (to retard degradation), then placed immediately on ice, transported to the laboratory, and stored at 4°C until analyzed.

VI. Data Analysis

Graphical displays will be used initially to examine spatial and temporal trends in pesticides concentrations as well as discharge and pesticide load information. In addition, a correlation matrix will be examined to identify relationships among the measured parameters. If feasible, a multivariate analysis (e.g. principal components analysis) will be conducted to aid in the identification of factors contributing to a majority of the variability seen in pesticide concentrations. Finally, pesticide loads will be calculated for each sampling point using pesticide concentrations and measured discharge. This calculation provides useful information about the transport of pesticides into and within the San Joaquin River.

VII. Quality Control and Chemical Analytical Methods

As a quality control measure, 10% of the water samples will be split for chemical analysis. Sites for split sample collection will be randomly selected from established monitoring sites. Blanks and spikes will also be submitted with field samples for analysis.

A newly-developed analytical screen for OPs and carbamates in water will be performed by Enseco-Cal Laboratory. Pesticides and their anticipated detection limits are listed in Table 1.

VIII. Time Table

Time Table For The First Sampling Year Only

Date	Activiy
Sept. 1990 to Jan. 1991	Chemical analytical development
March 1991 to Feb. 1992	Water and sediment sampling
March 1992	Chemical analysis complete
June 1992	Report Completion - first year only

IX. References

Anderson, S.W., T.C. Hunter, and J.R. Mullen. 1990. Water Resources Data, California, Water Year 1989. Vol.3. U.S. Geological Survey Water-Data Report CA-89-1. Sacramento, CA.

Clifton, D.G. and R.J. Gilliom. 1989. Sources and concentrations of dissolved solids and selenium in the San Joaquin River and its tributaries, California, October 1985 to March 1987. U.S. Geological Survey, Water-Resources Investigation Report 88-4217. Sacramento, CA.

Connor, V. 1988. Survey Results of the San Joaquin River Watershed Survey. CVRWQCB Memorandum dated March 10, 1988.

Fleck, J., L. Ross, and K. Hefner. 1988. Endosulfan and Chlorthal-dimethyl Residues in Soil and Sediment of Monterey County. CDFA Report EH 88-6.

Foe, C. 1989. Detection of pesticides in the San Joaquin River on 16 June 1989. CVRWQCB Memorandum dated Oct. 20, 1989.

Foe, C. 1990. Detection of pesticides in the San Joaquin watershed during February 1990. CVRWQCB Memorandum dated June 25, 1990.

Gilliom, R.J. and D.G. Clifton. 1990. Organochlorine pesticide residues in bed sediments of the San Joaquin River, California. Water Resources Bulletin 26(1):11-24.

Guy, H.P. and V.W. Norman. 1970. Field methods for measurement of fluvial sediment. In: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 3, Chapter C2, 59 p.

Shelton, L.R. and L.K. Miller. 1988. Water Quality Data, San Joaquin Valley, California. March 1985 to March 1987. U.S. Geological Survey Open-File Report 88-479. Sacramento, CA.

Table 1. Organophosphate and carbamate pesticides included in Enseco-Cal laboratory screens. Detection limits are 0.01 and 0.1 ug/L for organophosphates and carbamates, respectively.

Organophospates	Carbamates
Chlorpyrifos & oxon	Aldicarb, sulfoxide & sulfone
DDVP	Carbaryl
Dematon-S sulfone & sulfoxide	Carbofuran
Demeton-O, Demeton-S	Methiocarb, sulfoxide & sulfone
Diazinon	Methomyl
Dimethoate	Oxamyl
Disulfoton, sulfoxide & sulfone	
Ethoprop	
Fenamiphos, sulfoxide & sulfone	
Fensulfothion	
Fonofos & oxon	
Guthion & OA	
Malathion & oxon	
Methidathion	
Methyl Parathion & oxon	
Mevinphos (Phosdrin)	
Naled	
Parathion & oxon	
Phorate, sulfoxide & sulfone	
Phoratoxon, sulfoxide & sulfone	
Phosalone	
Phosmet & OA	
Sulfotepp	
Bensulide & OA	

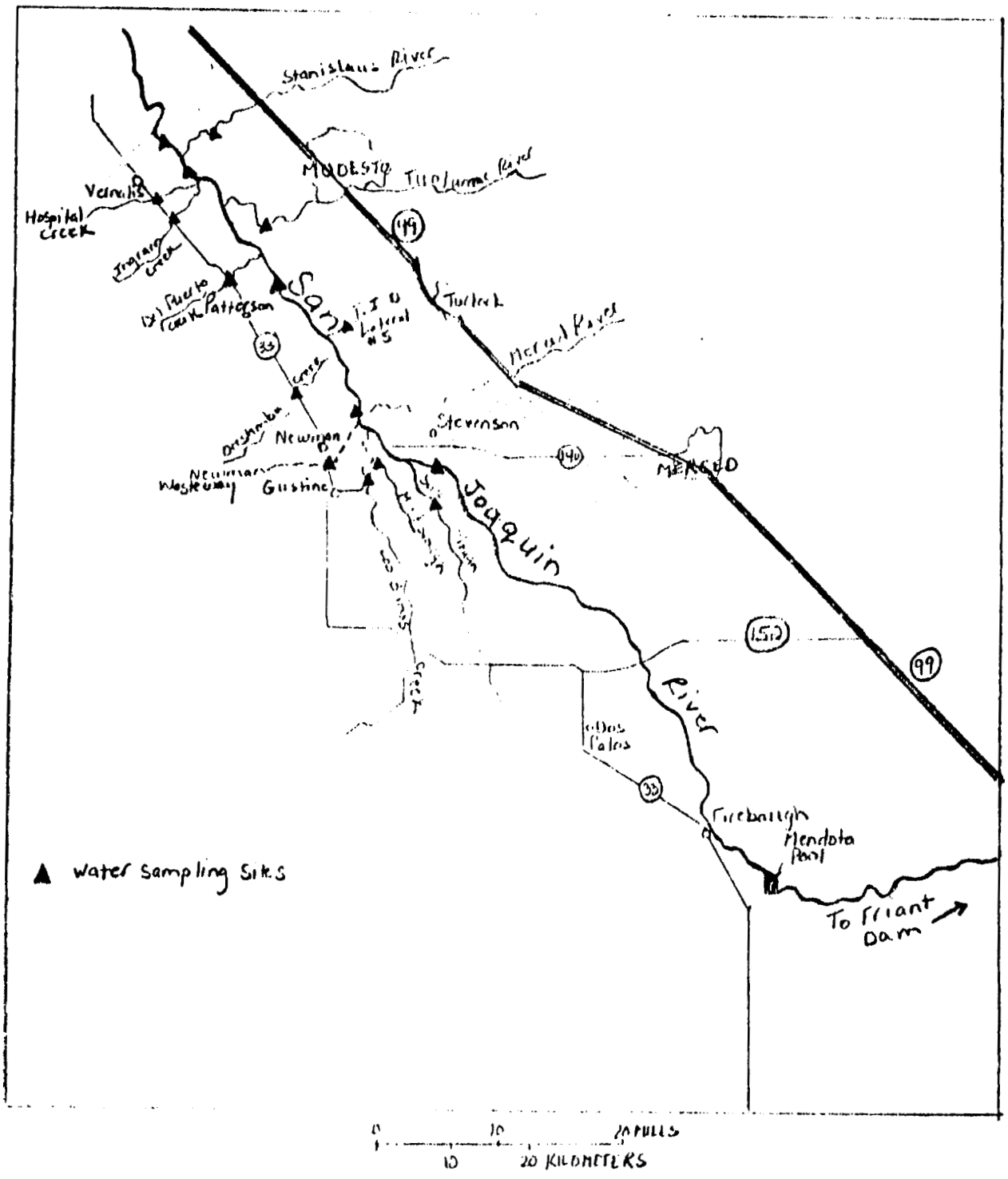

Figure 1. Location of proposed sampling sites in the San Joaquin River Watershed. Map copied from Clifton and Gilliom, 1989.