California Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1020 N Street, Room-A160
Sacramento, CA 95814
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FOUR RIVER MONITORING PROTOCOL

I. Introduction

This study is a cooperative effort between the Department of Pesticide Regulation (DPR) and the Department of Fish and Game (CDFG). The study is a field and laboratory investigation of pesticide residues in surface waters of four major rivers in California. It is part of the Department's effort to initiate a pilot surface water program to prevent contamination of surface waters in the state from pesticides. This protocol describes the field investigation to be done by DPR. A separate protocol describes the laboratory investigation being conducted by CDFG.

Pesticide residues in surface water are of concern to the Department of Pesticide Regulation and the Department of Fish and Game due to their possible effects on California's fish and wildlife. Studies conducted on the San Joaquin and Sacramento Rivers (Ross 1991 & 1992, Lee 1993, Shelton and Miller 1988, Anderson et al. 1989) indicate certain pesticides occur in these regions. In some of these studies, pesticide residues were detected at concentrations exceeding the U. S. EPA water quality criteria. These studies, however, were only conducted once per month or during certain seasons of the year. Also the biological significance from exceeding these criteria are largely unknown. A more consistent approach is required in order to identify potential problems caused by pesticides in the major river systems in California. Therefore, in this study, water will be collected weekly from one sampling site on each of four rivers for a one year period. In addition to measuring pesticide concentrations and basic water quality parameters, DPR will supply samples to the California Department of Fish and Game (CDFG) for determining toxicity to aquatic organisms. In this joint study, DPR will use the data collected to determine the temporal distribution of pesticide residues in the four rivers while CDFG will characterize aquatic toxicity (CDFG 1993). This study is not all-comprehensive, but pesticide and toxicity problems in surface waters can be discovered and remedial actions developed and implemented. The following describes the monitoring to be done by DPR. Another protocol will be issued by CDFG describing their toxicity test procedures.

II. Objective

To conduct a weekly survey for a period of one year on four rivers systems in California to identify the temporal distribution of organophosphate (including diazinon), carbamate, and other pesticides of high use which may be toxic to aquatic organisms.

This study will provide DPR's surface water program with baseline information which will contribute to the effective and efficient mitigation of adverse effects of pesticides on surface water quality.

III. Personnel

This project will be conducted by the Environmental Hazards Assessment Program (EHAP) under the general direction of Roger Sava, Senior Environmental Research Scientist (Supervisor). Key personnel are listed below:

Project Leader: Carissa Ganapathy
Field Coordinators: Adrian Bradley (Salinas River), Kevin Bennett (Merced River Watershed), Carissa Ganapathy (Russian river), Craig Nordmark (Sacramento River)
Senior Scientist: Lisa Ross
Study Design/Data Analysis: Terri Barry
Lab Liaison/Quality Control: Nancy Miller
Agency and Public Contact: Pat Dunn, phone: (916) 324-4100
Fax: (916) 324-4088

IV. Study Plan

The study plan is designed to provide necessary preliminary information for development of a longer-term program that will ensure that the potentially adverse effects of pesticide use on surface water quality will be addressed in the most efficient and effective manner.

Surface water from one site on each of four rivers (Sacramento, Merced, Russian and Salinas Rivers) in California will be sampled weekly for one year. This information will be used to determine the seasonal occurrence of pesticides in these rivers. Surface water will be composited during a 2 to 3-day sampling period using an autosampler. Samples will be distributed to the California Department of Food and Agriculture (CDFA) laboratory for chemical analyses and to CDFG for toxicity tests.

The location of the sites will be determined by DPR and DFG staff after consultation with the Regional Water Quality Control Boards and the local County Agricultural Commissioner and analysis of land and pesticide use. Sampling sites will be located downstream from agricultural areas and upstream from major sources of dilution water. Sampling sites must also be located in areas of the river that are well mixed. Autosamplers will be placed in or near United States Geological Survey (USGS) or California Department of Water Resources (DWR) gaging stations so that water discharge can be recorded. Gaging stations sites are preferable because they provide accessibility, availability of electrical power, protection from vandalism, and may supply data on specific conductance, temperature and pH in addition to discharge. If a gaging station is not available, placement of autosamplers along each river will require a secure location that is accessible by sampling personnel, fairly level so the jars fill equally, and is near a power supply. Also, to reduce suction and purging time through the sampling lines, the sampler should be located as close as possible to the river.

Samples will be analyzed for organophosphate and carbamate pesticides included in the CDFA laboratory screens (Table 1). From each screen concentrations of individual analytes will be determined. In addition, endosulfan I, II and sulfate will be included for analysis. Additional pesticides may be selected for analysis based on the quantity used, aquatic toxicity, and bioaccumulation potential.

In addition to pesticide residue analysis, sample splits will be sent to the California Department of Fish and Game (CDFG) for aquatic toxicity testing. CDFG will characterize aquatic toxicity using EPA methods. In addition, CDFG will analyze the water samples for total ammonia, akalinity, hardness, and specific conductivity.

V. Sampling Methods

At each sampling site, water will be collected with an ISCO model 2700R/2740® refrigerated automatic sampler. The autosampler will be programmed to collect 18-liters of water every week. The 18-liters will be a composite of hourly sub-samples collected during a 2 to 3-day sample period within each week. The water sample will be split into 1-liter bottles for shipping and storage. Approximately 3 to 5 liters will be sent to the CDFA laboratory for pesticide analyses and 13 to 15 liters will be sent to CDFG for aquatic toxicity tests and water quality analysis.

Other parameters to be measured in situ are temperature, dissolved oxygen, and pH. If a sampling site is not located near a gauging station that collects these data, then measurements will be taken once a week when the composite sample is collected. Amber-glass sample bottles will be capped with Teflon-lined lids and placed on wet ice (4°C) for delivery to the CDFA laboratory for analysis. The organophosphate and carbamate samples will be acidified with HCL to a pH of 3.0 to 3.5, after the samples are placed in 1-liter bottles. Acidification is done to retard degradation of these organophosphate and carbamate pesticides during shipping and storage. In contrast, the endosulfan/diazinon samples will not be acidified since these pesticides are best preserved under neutral conditions. In addition, CDFG samples will not be acidified prior to aquatic toxicity testing except for the 0.45 liters needed for the total ammonia and hardness tests.

During the year long study, a total of 687 water samples will be analyzed for pesticide residues (4 river sites x 3 screen analyses x 52 weeks + 63 QC split analyses).

VI. Chemistry methods

Organophosphate and carbamate pesticides as well as endosulfan and diazinon will be analyzed using methods previously developed by the CDFA laboratory for other surface water studies (Table 1). For each individual river, additional pesticides may be selected for analysis based on the quantity used, aquatic toxicity and bioaccumulation potential.

VII. Quality control

As a quality control measure, approximately 10% of the samples collected will be split and analyzed as replicates by CDFA. Blind spikes and blanks will also be submited throughout the study as continuing quality control.

VIII. Timetable

This study will begin on the Sacramento and Merced Rivers in November and December of 1993. Sampling on the Russian and Salinas will follow in February and March of 1994. Reports will be produced quarterly, and the final combined report will be completed by June 1995.

Work	Sacramento River	Merced River	Russian River	Salinas river
site survey	Sep 1993	Sep 1993	Oct 1993	Nov 1993
site preparation	Nov 1993	Dec 1993	Feb 1994	Mar 1994
begin sampling	Nov 1993	Dec 1993	Feb 1994	Mar 1994
1st quarter report	Mar 1994	Apr 1994	Jun 1994	Jul 1994
2nd quarter report	Jun 1994	Jul 1994	Aug 1994	Sep 1994
3rd quarter report	Sep 1994	Oct 1994	Nov 1994	Dec 1994
finish sampling	Nov 1994	Dec 1994	Feb 1995	Mar 1995
4th quarter report	Jan 1995	Feb 1995	Apr 1995	Mar 1995

Final combined report by June 1995.

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.

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.

Lee, J.M., L.J. Ross and R.G.Wang. 1993. Integrating Environmental Toxicology and Monitoring in the Development and Maintenance of a Water Quality Program: California's Rice Herbicide Senario. In: Effective and Safe Waste Management. Chapter 18. Lewis Publishers. p211-224.

Ross, L.J., 1991. Preliminary results of the San Joaquin River study; March and April 1991. Memorandum to John Sanders, Environmental Hazards Assessment Program. Department of Pesticide Regulation. November 4, 1991.

Ross, L.J., 1992. Preliminary results of the San Joaquin River study; Winter 1991-92. Memorandum to Kean Goh, Environmental Hazards Assessment Program. Department of Pesticide Regulation. May 22, 1992.