California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1020 N Street, Room 161
Sacramento, California 95814
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1995 RICE PESTICIDES MONITORING PROTOCOL

I. Introduction

In the late 1970's and early 1980's, fisheries biologists from the California Department of Fish and Game (CDFG) observed extensive fish kills, involving primarily carp, in some agricultural drains in the rice growing region of the Sacramento Valley. Investigations from 1980 to 1982 by CDFG resulted in the determination that these fish kills were due to toxicity related to the rice herbicide, molinate (Ordram®) (Finlayson et al. 1982). In addition, during the summers of 1981 and 1982, the City of Sacramento also received numerous complaints about the taste of the city drinking water and later determined that the cause was another rice herbicide, thiobencarb (Bolero®) (California 1987). These pesticide related incidents were of major concern because the water in the drains is affected by agricultural practices in the Sacramento Valley, and pesticide residues in these waters contribute to the mass load of pesticides in the Sacramento River.

In an effort to mitigate these problems, CDFG, the California State Water Resources Control Board, the Central Valley Regional Water Quality Control Board, the California Department of Pesticide Regulation (DPR), formerly the California Department of Food and Agriculture (CDFA) (Division of Pest Management), county agricultural commissions and private industry are participating in a project to reduce the presence of rice pesticides in the surface waterways of the Sacramento Valley. Currently, molinate, thiobencarb, carbofuran (Furadan®), methyl parathion and malathion concentrations and water quality parameters are monitored in the agricultural drains of the Sacramento Valley each year. Surface water samples used for analyses of rice chemical concentrations were collected during the rice growing season by CDFG from 1980 to 1994 and will now be collected by DPR. CDFG will continue to perform biotoxicity testing; toxicity results will be provided by CDFG in a separate report.

During 1994 monitoring, the concentration of each of the rice pesticides – molinate, thiobencarb, carbofuran, methyl parathion and malathion – exceeded the recommended water quality performance goals for at least one of the four monitoring sites; the highest concentrations consistently occurred at the Colusa Basin Drain site number 5 (Lee 1994). Since the rice pesticide concentrations were highest at the Colusa Basin Drain site number 5 (CBD5) and because there is an established historical record of these concentrations, CBD5 will be used exclusively as a rice pesticides indicator site for the 1995 Rice Pesticides Monitoring Program.

In addition to measuring pesticide concentrations and water quality parameters, DPR will also collect water for CDFG's biotoxicity tests. The data collected in this study on pesticide residues will be used to evaluate the success of the 1995 Rice Pesticide Monitoring Program and develop any programmatic changes for the 1996 Program.

II. Objective

The Colusa Basin Drain is important to the Rice Pesticides Monitoring Program for several reasons: (1) it receives a large volume of rice field effluent from the Sacramento Valley, (2) previous water quality data has been collected along its watercourse and (3) it is a tributary of the Sacramento River. The objective of this study is to measure the concentrations of five pesticides – molinate, thiobencarb, carbofuran, methyl parathion and malathion – in the Colusa Basin Drain.

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/Field Coordinator: Kevin Bennett
Senior Scientist: Lisa Ross
Data Analysis: Rosie Gallavan
Quality Assurance/Control: Nancy Miller
Agency and Public Contact: Marshall Lee

Questions concerning this monitoring project should be directed to Marshall Lee at (916) 324-4100.

IV. Study Plan

Rice pesticides are monitored in the Colusa Basin Drain because it is a major agricultural drain discharging to the Sacramento River. CBD5 represents a culmination of most of the drainage from rice growing regions west of the Sacramento River. Data from previous studies (Lee 1994b, Lee and Gorder 1993 & 1992) have shown that significant rice pesticide concentrations in the Sacramento Valley are consistently found at CBD5. Water flowing past CBD5 represents a large percentage of rice field effluent for the Sacramento Valley, and this site has historically been used to monitor pesticide residues for the Rice Pesticides Monitoring Program. CBD5 was chosen as the sole monitoring site for 1995 because samples collected at this site have historically yielded the highest pesticide detections when compared to the other sites; the assumption being that if water quality performance goals are met at CBD5, they will be met elsewhere in the region.

The monitoring program will begin with background sampling in mid-April. Surface water sampling and water quality measurements will be performed twice weekly for a period of approximately ten weeks following initial field flooding. The predicted sampling schedule is presented below:

DATE	SITE (CBD5)	
	Day 1	Day 2
Background (2 to 3 weeks prior)	Ia	IIb
Week 1	I	II
2	I	II
3	I	II
4	I	II
5	I	II
6	I	II
7	I	II
8	I	IIIc
9	I	III
10	I	III

a) Schedule I: molinate, thiobencarb, carbofuran, methyl parathion and malathion + quality control set for all chemicals.
b) Schedule II: molinate, thiobencarb, carbofuran, methyl parathion and malathion + biotoxicity.
c) Schedule III: schedule I less quality control set.

Estimated number of samples:

DATE	MOLINATE	THIOBENCARB	CARBOFURAN	METHYL PARATHION & MALATHION†	BIOTOXICITY
Background	2(1)	2(1)	2(1)	2(1)	1
Week 1	3 (1)‡	3 (1)	3 (1)	3 (1)	1
2	3 (1)	3 (1)	3 (1)	3 (1)	1
3	3 (1)	3 (1)	3 (1)	3 (1)	1
4	3 (1)	3 (1)	3 (1)	3 (1)	1
5	3 (1)	3 (1)	3 (1)	3 (1)	1
6	3 (1)	3 (1)	3 (1)	3 (1)	1
7	3 (1)	3 (1)	3 (1)	3 (1)	1
8	3 (1)	3 (1)	3 (1)	3 (1)	0
9	3 (1)	3 (1)	3 (1)	3 (1)	0
10	3 (1)	3 (1)	3 (1)	3 (1)	0
TOTALS	**32 (11)**	**32 (11)**	**32 (11)**	**32 (11)**	**8**

†) Methyl parathion and malathion are analyzed from a single sample.
‡) Numbers in parentheses indicate the number of samples taken for quality control under schedule I.

Total Chemical Analyses = 128 samples

Biotoxicity(1 sample/wk x 8 wks) = 8 samples

Total = <u>136 samples</u>

The biotoxicity samples and backups will be collected as part of the primary volume of water. Two un-acidified and acidified backup samples each will be collected and stored. All backups will be held in storage (4°C) until the initial data analysis is complete.

Water pH, temperature and dissolved oxygen will be measured *in situ,* at each site, during individual sampling periods.

V. Sampling Methods

A cross-sectional water sample will be collected using the equal-width-increment sampling method (Edwards and Glysson 1988) which requires equal spacing of a number of sampling points across the drain based on its width and flow. This method utilizes a depth-integrated sampler (DH-76) with a 3-liter Teflon® bottle and nozzle, nylon rope and stainless steel buckets as its sampling components. As the cross-sectional sampling proceeds, the sample will be composited temporarily in a stainless steel bucket until the appropriate volume of water has been collected. Then using a 10-port splitter (Geotech, model Dekaport), the water sample will be split into amber glass bottles and sealed with Teflon®-lined lids. Samples to be analyzed for carbofuran, methyl parathion and malathion will be acidified on site with 3N HCl to a pH between 3.0 and 3.5 for increased sample stability during storage. All samples will be stored on wet or blue ice (4 °C) until delivered to the laboratory for analyses.

Every attempt will be made to avoid both disturbing the bottom of the agricultural drain and sampling areas of the drain with no observable flow. As standard operating procedure, all sampling personnel will wear rubber gloves during sampling and if contamination is suspected, the gloves will be replaced.

Water temperature and pH will be measured with a Sentron pH/temperature meter (model 1001), and dissolved oxygen will be measured with a YSI (Yellow Springs Instrument) dissolved oxygen meter (model 57). Flow rates for CBD5 are available from a nearby gauging station and will be used to predict the mass loading of the five pesticides in the Colusa Basin Drain.

VI. Chemical Analysis and Biotoxicity

Chemical analysis for molinate and thiobencarb will be performed by Zeneca Agricultural Products and Morse Laboratory (under contract with Valent USA) respectively. FMC Corporation will perform the chemical analysis for carbofuran, and the California Department of Food and Agriculture (CDFA) Laboratory Services will perform the analysis on both methyl parathion and malathion. The method detection limit (MDL) is defined as the lowest concentration of analyte that the method can detect
reliably in a matrix blank. The MDLs for the monitoring program are listed below:

	µg/L
Molinate (Zeneca) -	1.0
Thiobencarb (Morse) -	0.5
Carbofuran (FMC) -	0.4
Methyl parathion (CDFA) -	0.05
Malathion (CDFA) -	0.05

These MDLs may be lowered pending continuing laboratory contract negotiations. Chemical analytical methods will be provided in the final report.

CDFG's Aquatic Toxicology Laboratory (ATL) will determine toxicity using a 96-hour bio-assay with cladocerans. Percent survival of test organisms in undiluted sample water will follow current U.S. Environmental Protection Agency guidelines.

VII. Quality Assurance/Control

As an inter-laboratory quality control measure, a minimum of 20% of the samples collected will be analyzed by CDFA for molinate, thiobencarb and carbofuran to verify results by Zeneca, Valent (Morse) and FMC. Also, a minimum of 20% of the samples collected will be analyzed for methyl parathion and malathion by a contract laboratory. Rinse blanks, blind matrix spikes and blanks will be submitted throughout the study under the auspices of the Quality Assurance Officer as continuing quality control. Details of EHAPs quality assurance program are available upon request and will be included in the final report.

VIII. Time Table

This study will be conducted at the start of the 1995 rice pesticide application season which typically begins during the month of April or May and will consist of the following:

Field Sampling - May through July 1995

Chemical and Toxicity Analysis - May through August 1995

Preliminary Report - September 1995

Final Report - November 1995

IX. References

California Department of Health Services. 1987. Proposed Maximum Contaminant Level, Thiobencarb (Bolero®). Hazard Evaluation Section, Berkeley.

Edwards, T.K. and D.G. Glysson. 1988. Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531. Page 118.

Finlayson, B.J., J.L. Nelson and T.L. Lew. 1982. Colusa Basin drain and reclamation slough monitoring studies, 1980 and 1981. California Department of Fish and Game, Environmental Services Branch, Administrative Report No. 82-3.

Lee, J.M. 1994. Personal communication between J.M. Lee and K.P. Bennett. California Department of Pesticide Regulation, Environmental Monitoring and Pest Management. September 8, 1994.

Lee, J.M. 1994b. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks, Executive Officer, California Regional Water Quality Control Board, Central Valley Region. California Department of Pesticide Regulation, Pest Management Assessment Program. March 8, 1994.

Lee, J.M. and N. Gorder. 1993. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks, Executive Officer, California Regional Water Quality Control Board, Central Valley Region. California Department of Pesticide Regulation, Pest Management Assessment Program. January 29, 1993.

Lee, J.M. and N. Gorder. 1992. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks, Executive Officer, California Regional Water Quality Control Board, Central Valley Region. California Department of Pesticide Regulation, Pest Management Assessment Program. February, 1992.

X. Budget

Personnel	
(21 days x 8 man.hrs/day x $18.75/man.hrs)	= $ 3,150
Staff Benefits (10.735%)	= $ 338
Total Personnel Services	= $ 3,488
Operating Expenses	
Supplies/Services (bottles & shipping)	= $ 450
Vehicles (1,680 miles x $0.26/mile)	= $ 437
Total Operating Expenses	= $ 887
Chemical Analyses and Biotoxicity	
Molinate ($300/sample x 21 samples) ($ incurred by Zeneca)	= $ 0
Thiobencarb ($300/sample x 21 samples) ($ incurred by Valent)	= $ 0
Carbofuran ($300/sample x 21 samples) ($ incurred by FMC)	= $ 0
Methyl parathion, Malathion ($300/sample x 21 samples)	= $ 6,300
Continuing QC (104 samples x $300/sample)	= $ 31,200
Bioassay ($110/sample x 8 samples)	= $ 880
Total Chemical Analyses and Biotoxicity	= $ 38,380
TOTAL	***= $ 42,755***