California Department of Pesticide Regulation
Environmental Monitoring and Pest Management
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Protocol for Toxicity Monitoring in Rice Recirculating Systems

I. Introduction

The Central Valley Regional Water Quality Control Board (CVRWQCB) monitored emergency water releases from rice fields in 1993 (CVRWQCB 1993). The emergency releases were made 6 to 17 days after molinate and 14 to 41 days after carbofuran applications. Samples from fields treated with both pesticides were all toxic to Ceriodaphnia dubia in toxicity tests. This generated concern about resultant toxicity in drainage canals of recirculating systems receiving such runoff.

Water releases from rice fields treated with carbofuran and molinate are allowed after a 28-day post-application hold. Prior to 1994, emergency releases were allowed in rice fields of non-recirculating systems after 7 days. Since 1994, emergency releases have not been permitted. In contrast, water from rice fields in recirculating irrigation systems still may be released 8 days after application of both pesticides, even in non-emergency situations. Given the results from the CVRWQCB toxicity test, it is possible that water in recirculating systems may be toxic to aquatic life. Therefore, this study is being conducted to monitor water in recirculating systems for toxicity using Ceriodaphnia dubia.

II. Objectives

1. To assess the toxicity of rice field release water after two application methods for carbofuran.

2. To assess the toxicity of canal water in recirculating irrigation systems during rice field water releases.

III. Personnel

This study will be conducted by personnel in the Environmental Hazards Assessment Program, under the general direction of Don J. Weaver, Senior Environmental Research Scientist. Key personnel are listed below.

Project Leader - David Kim
Senior Scientist - Lisa Ross
Lab Liaison / Quality Assurance - Nancy Miller
Data Analysis - Rosie Gallavan
Public and Agency Contact - Marshall Lee

Questions concerning this monitoring program should be directed to Marshall Lee at (916) 324-4100, FAX (916) 324-4088.

IV. Study Plan

Rice fields and canals will be selected in multi-farm recirculating systems. To satisfy the first study objective, two methods of carbofuran application will be monitored, a post-flood "Leathers" method and a pre-plant incorporation of carbofuran. The Leathers method is a post-flood application where the rice field is flooded, seeded, then the water level is lowered and carbofuran applied. The field is then reflooded and the water held for a minimum of 8 days. However, molinate is usually applied during the required 8 day carbofuran hold, and thus water cannot be released until at least 8 days after the molinate application. In the pre-plant incorporation method, carbofuran is applied, the field is flooded then seeded. Molinate is often applied after the 8 day carbofuran hold, thus water may be released, but not typically, prior to the molinate application. For this study only fields treated with both molinate and carbofuran, with no water releases between applications, will be examined.

Twelve fields, six post-flood application and six pre-plant incorporation, will be monitored. Two samples will be taken from rice field release water after both carbofuran and molinate are applied. These two samples will be collected as replicates to be used in an analysis of variance. Water samples will be collected from the field discharge point within 24-hours of the initiation of water release. This water will be assumed well mixed and collected as a grab sample. Background samples for the "Leathers" method will be collected from rice field water prior to pesticide applications. For the pre-plant incorporation method, field inlet water will be used.

To satisfy objective two, release water from four fields that have had both pesticides applied, will be monitored as it flows through a recirculating system. The same parcel of water, including the discharge water, will be sampled as it moves from the field, through the canals, to the bottom of the recirculating system. Water samples will be collected below the confluence of all canals, up to a maximum of 12 sampling sites. Flow rates at each

sampling site will be measured to calculate pesticide loads and determine appropriate sampling intervals. A water sample will also be collected upstream of the discharge point of each sampled field during release, to determine the pesticide concentrations upstream of the discharge point. In addition a maximum of four background samples will be collected at the inlets to the recirculating system examined in this objective.

Estimated number of samples:

Objective 1.

Discharge

12 fields x 2 replicates = 24 samples

Background, Field

12 fields x 1 sample = 12 samples

Objective 2.

Canal

4 fields x 1 sample x 12 sampling sites (estimate) = 48 samples

Background, System

Inflow to system x 4 samples = 4 samples

Quality Control.

Quality Control Splits

10% of total samples collected = 9 samples

total = 97 samples

Laboratory tests will include acute toxicity, Toxicity Identification Evaluation (TIE), and analysis for molinate, thiobencarb, carbofuran, methyl parathion, malathion, filterable or dissolved copper, and any other rice pesticide used in the closed system prior to sampling. Field water quality measurements will include pH, electroconductivity (EC), temperature, ammonia, and dissolved oxygen (DO). Information on pesticide use in monitored fields will be recorded.

V. Sampling Methods

A sample will consist of ten liters of water collected at each site. Samples will be split with a ten port splitter (USGS designed) into eight 1-liter amber glass bottles with Teflon® lined caps. Four of the one-liter splits will be used for chemical analysis, three for toxicity testing and TIE, and two for backups (see section VII). All canal water samples will be collected using a hand held water sampler and the equal-width increment, depth integration method (Guy and Norman 1970).

Water pH and temperature will be measured with a Sentron pH/temperature meter (model 1001). EC will be measured with a YSI (Yellow Springs Instrument) salinity-conductivity-temperature meter (model 33), and DO with a YSI dissolved oxygen meter (model 57). Ammonia will be measured using an ammonia-nitrogen test kit made by

CHEMetes (model AN-10).

Samples for carbofuran analysis will be acidified with 3N HCl to a pH of 3 to 4 for increased stability during storage (Miller 1991). All samples will be stored and shipped on wet ice and refrigerated @ 4oC until analyzed.

VI. Data Analysis

For objective one, an analysis of variance will be used to test for differences between release water of the two management practices. The two variables to be analyzed are chemical concentration and percent mortality. The following nested experimental design will be used:

ANOVA

Source	df
Management Practice	1
Fields/Management Practice	10
Samples/Fields	12
Total	23

The data is classified according to management practice, then within management practice according to field, then within field according to sample. The source of variation for fields within management practice will provide an estimate for experimental error. In order to satisfy the required assumptions for the analysis of variance, a transformation may be necessary for the mortality data since it is reported on a percentage basis.

Objective two, toxicity of canal water within a recirculating irrigation system, will be assessed qualitatively.

VII. Toxicity/Chemical Analysis

A 96-hr toxicity test using Ceriodaphnia dubia will be started on samples within 36 hours of collection. A TIE will be performed on toxic samples (a maximum of seven samples). Chemical analysis will include molinate, thiobencarb, carbofuran, methyl parathion, malathion, and dissolved copper. Toxicity tests and dissolved copper analyses will be performed by California Department of Fish and Game laboratories. The remaining samples will be analyzed by the California Department of Food and Agriculture Chemistry Laboratory. The quality control split samples will be analyzed by contract laboratories.

The ten one-liter samples will be analyzed as follows;

3 liters for acute toxicity and TIE tests

1 liter for thiocarbamates

1 liter for carbofuran (acidified to pH 3-4)

1 liter for organophosphorous pesticides

1 liter for dissolved copper

1 liter backup, acidified

1 liter backup, non-acidified

Blanks and spikes will be submitted periodically with field samples for quality control.

VIII. Time Table

Field Sampling - May - June 1995

Chemical Analysis - May - July 1995

Report - September 1995

IX. References

California Regional Water Quality Control Board - Central Valley Region, 1993. Molinate Concentrations in Rice Field Discharges, 1993. Memorandum from Rudy Schnagl and Wendy Wyels to Marshall Lee. August 6, 1993.

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, 59p.

Miller, Nancy. 1991. Study X87 - Storage Stability Study for Carbofuran. California Department of Food and Agriculture Chemistry Laboratory - in house study.