California Department of Food and Agriculture
Environmental Monitoring and Pest Management
1220 N Street, Room A-149
Sacramento, CA 95814

March 25, 1988

PROTOCOL TO EXAMINE POTENTIAL SOURCES OF CARBOFURAN RESIDUES IN THE COLUSA BASIN DRAIN

I. INTRODUCTION

As part of a continuing program to protect the quality of water in the Sacramento River and associated drains, the Department of Fish and Game conducts yearly sampling for pesticides used in rice fields. In 1987, residues of carbofuran (Furadan®) were found at five of the six monitoring sites. Carbofuran residues were found most consistently and at highest concentrations in May and early June in the Colusa Basin Drain [1], a large drain contributing a major portion of irrigation return flow to the Sacramento River. Carbofuran is a systemic insecticide used against rice water weevil and sugar beet root maggot in rice and sugar beet fields, respectively. These two key crops, rice and sugar beets, appear to be major sources of carbofuran residues based upon the number of acres grown in the area and the amount of carbofuran applied [2]. In response to this problem, the Environmental Hazards Assessment Program (EHAP) will conduct a study to assess the amounts of carbofuran moving off-field in irrigation runoff water from rice and sugar beet fields.

II. OBJECTIVES

1. To estimate the mass of carbofuran moving off-site in irrigation runoff water from rice and sugar beet fields. From these data, it can then be determined if runoff water from irrigation of rice and/or sugar beets is the probable source of carbofuran residues in the Colusa Basin Drain.

2. To determine dissipation rates of carbofuran in water and soil of rice fields located in the Sacramento Valley.

3. To examine the contributions of carbofuran residues from three major tributary drains which receive runoff water from agricultural lands and discharge directly into the Colusa Basin Drain.

III. PERSONNEL

This study will be conducted by personnel from the Environmental Hazards Assessment Program. The overall supervisor will be John Sanders. Other key personnel involved in this study include:

Project Leader, Study Design/Data Analysis- Susan Nicosia

Senior Staff Scientist- Lisa Ross

Field Operations- Nancy Carr and David Gonzales

Lab Liaison/Quality Control- Nancy Miller

Agency and Public Contact- Madeline Ames

IV. STUDY PLAN

OBJECTIVE 1:

Field Sites

Three rice fields and three sugar beet fields will be selected from available fields located in Glenn, Colusa or Yolo Counties on the west side of the

Colusa Basin Drain. The criteria used to select fields will include: 1) similarity in size; 2) proximity to the source of irrigation water so as to reduce the potential for influx of carbofuran into the test fields from recycled water; and 3) presence of only one irrigation water inlet and only one outlet. Participating growers must be willing to allow installation of flow monitoring equipment at or near the field water outlet.

Farm practices taken into consideration for field selection will include: method of application, application rate, method of irrigation (for sugar beets) and use of pesticides other than carbofuran which will be applied to the field (i.e., herbicides applied to rice).

Pesticide Applications:

Rice - Carbofuran will be applied pre-flood to rice fields in granular form at an expected rate of 10 lbs./acre (0.5 lbs. ai/acre). Based on fields selected, applications will be made either by ground or aerial equipment. Application efficiency will be measured if aerial applications are made.

Sugar beets - Carbofuran will be applied to sugar beet fields by ground equipment at label rates (to be determined) at the time of planting.

For all ground applications, rates will be measured indirectly in the field by determining the weight of carbofuran granules used to fill the tank during the period of application, and by determining the actual percent of active ingredient in granules sampled from the bags which were used. A total of 5 composite samples will be collected at each field.

Sampling:

Prior to pesticide application, background surface soil samples will be taken from all fields. A total of 6 composite samples will be collected from each field.

Water samples will be collected at the inlet and outlet sites of each field and analyzed for concentrations of carbofuran. Sampling schedules for rice and sugar beets will be as follows:

Rice - Applications of carbofuran to rice fields are expected in April. After applications, the fields will be flooded and seeded. Some spillage of water from the fields is expected during the initial flooding period (early mid-April). Approximately 10-15 days after seeding, the herbicide Ordram® will be applied and water will be held for a 12 day period. After the herbicide holding period has ended (late April-mid May), continual water release can be expected until harvest. Depending upon grower discretion, a second herbicide (MCPA) may be used. The fields will be drained prior to MCPA application. Once the fields are reflooded, water will again be continuously released. To measure concentrations of carbofuran in run-off during these periods of water release, the schedule in Table 1 will be used. Sampling dates and intervals are only approximations and will depend upon grower management practices.

Table 1. Runoff Sampling Schedule for Rice Fields

Approximate Dates	Water Release Period	Sampling Interval	No. Samples Inlet	No. Samples Outlet	No. Fields	Total Samples
Apr. 15-19	1 (flood fields)	5 days	1/day	3/day	3	60
May 11	2 (post Ordram®)	9 days	1/day	2/day	3	81
May 21 till June 30	continuous release of water	next 3 weeks	2/week	1/day	3	81
		next 2 weeks	2/week	2/week	3	24
					TOTAL	246

Sugar beets - Applications of carbofuran to sugar beet fields are expected in early May. Carbofuran is applied with the seed and is immediately followed by irrigation for a 3-5 day period. The second irrigation is expected within the following 1-3 weeks. Subsequent irrigations are expected at 2-3 week intervals throughout the summer. To measure concentrations of carbofuran moving off-field during these periods of irrigation, the schedule in Table 2 will be used. The sampling dates and number of days per irrigation event are approximations dependent upon grower management practices.

Table 2. Runoff Sampling Schedule for Sugar Beet Fields

Approximate Dates	Irrigation Event	No. Days Event	No. Samples/Day Inlet	Outlet	No. Fields	Total Samples
May 1	1	5	1	4	3	75
May 10	2	5	1	3	3	60
May 25	3	5	1	3	3	60
June 10	4	5	1	1	3	30
June 25	5	5	1	1	3	30
					TOTAL	255

Flow of irrigation water off the fields will be measured continuously through the use of V-notch weirs and Stevens stage recorders installed at field water outlets. This will provide information on the volume of runoff water so mass discharge can be estimated.

Carbofuran residues in suspended sediment from runoff water will be measured at two times during the study. Two replicate samples will be taken from each field during the first two irrigation events in sugar beets and during the first two periods of water release in rice.

OBJECTIVE 2:

Dissipation of carbofuran from soil and water in rice fields will be measured by sampling these media in the bottom pad of each field once it has been flooded following the schedule outlined in Table 3. Day 0 is considered to be the first day the bottom pad is flooded to a depth of 1 inch (2.5cm) or greater and may be between 1 and 4 days after application of carbofuran.

Table 3. Carbofuran Dissipation Sampling Schedule for Rice Fields

No. Days Post-Flood	No. of Samples	No. of Fields	Matrix	Total Samples
0,1,2,4,6,8, 12,16,20,24,28	3 (replicates)	3	Water	99
0,2,6,12,20, 28,36,44,52	3 (replicates)	3	Soil	81
			Total	180

For objectives 1 and 2, additional measurements of the following parameters will be made:

Background soil - wet weight, percent moisture, pH, texture analysis, percent organic matter, and bulk density

Paddy soil - wet weight, percent moisture, and pH

Water - pH, temperature (rice and sugar beets) and depth in rice pads

Air - temperature.

OBJECTIVE 3:

Agricultural Drain Water:

All field sampling and sample analyses for this portion of the study will be conducted by the Department of Fish and Game in conjunction with their ongoing monitoring of rice herbicides in agricultural drain water.

Three major agricultural drains which discharge directly into the Colusa Basin Drain will be selected for periodic sampling based upon: (1) the volume of

drain outflow to the Colusa Basin Drain, and (2) the volume of agricultural drainage water received.

Two replicate samples will be collected from each drain on 6 occasions (bimonthly) during the study period and analyzed for carbofuran and two toxic metabolites, 3-keto carbofuran and 3-hydroxy carbofuran.

Statistical Methods:

The nature of the degradation of carbofuran in soil and water will be explored using both linear and nonlinear regression techniques. With respect to nonlinear regression techniques, a first order exponential decay model of the following functional form $f(t) = B_o e^{-Bt}$ +e will be examined where B_o is the initial peak concentration after flooding and B is the decay constant.

The mass discharge of carbofuran from rice and sugar beet fields will be estimated by computing a weighted daily average of volume of runoff times carbofuran concentration. The relative contribution of carbofuran to the agricultural drains from rice and beets will be descriptive in nature. The limited number of fields available for study precludes the use of any formal statistical procedures.

IV. SAMPLING METHODS

Background Soil - Background surface soil samples will be collected using metal soil corers to a depth of 4 inches (10 cm). Six samples will be collected from each field. Each sample will be a composite of 12 cores taken from randomly selected sites within each field. Immediately after collection, soil samples will be placed on dry ice. Samples will remain frozen until they are analyzed.

Runoff Water - Water samples will be collected from inlet and outlet sites of sugar beet and rice fields. Inlet water from sugar beet and rice fields will be sampled from source canals or ditches at the field entry points. Outlet water will be collected directly from water flowing over the drain weirs; when water is not flowing over the drain weirs, any water seeping out will be collected.

Water will be collected in 1 liter amber glass bottles at all sites (rice, sugar beets) using a hand pump. The pH of the water will be determined and sulfuric acid will be added to acidify samples to pH 2.5-3.5 3. Bottles will be sealed with aluminum foil-lined caps and placed on wet ice. Samples will remain refrigerated until they are analyzed.

Runoff Sediment: Runoff water samples will be collected from sugar beet and rice fields and analyzed for the fraction of carbofuran in water and suspended sediment.

Water Flow:

Flow of irrigation water off the field will be measured using V-notch weirs and Stevens stage recorders installed at field outlets. Continuous measurements of water height will be recorded on seven day charts. Data from these charts will be used to calculate the volume of runoff water.

Dissipation: Soil and water will be collected from the bottom pad in each rice field. Within each bottom pad, 3 composite samples will be collected for each matrix. Sampling will be stratified** by dividing each pad into 6 sections. ~~Two~~ 1 subsamples will be collected from random sites within each section (~~12~~ 6 subsamples total) and composited into a sample. Sampling sites

will be located 15 feet in from the paddy levees and banks to avoid edge effects. All samples for each matrix will be collected in this manner. Water samples cannot be taken immediately after application since it can take up to 5 days to flood the fields. However, samples can be taken once water reaches 1 inch (2.5 cm) in the pad. Once collected, samples will be handled as specified in soil and water sections above.

Pesticide Application:

On the day of application in sugar beet fields, the total weight of carbofuran granules applied to each field will be determined by weighing the bags of carbofuran used to load the tank and weighing any granules left after application. In rice, the weight of carbofuran granules applied to the fields will be determined by a 2-step process. First, the total weight of granules applied to all pads except the bottom pad in a field will be measured (using the above method). Second, a separate measurement of the total weight of granules applied only to the bottom pad of the field will be made. This procedure will allow an accurate determination of the amount of carbofuran applied in bottom pads and is needed to measure dissipation of this pesticide in rice fields.

The percent active ingredient in the granule formulation will be determined for each tank load by taking a composite sample. Samples weighing 10-50 grams will be taken from each of several bags used to load the tank and combined to give approximately a 200 gram composite sample. A total of 5 composite samples will be collected at each field.

VI. CHEMISTRY METHODS/QUALITY CONTROL

Analytical methods are currently being developed for the detection of carbofuran using gas chromatography and liquid chromatography. Analyses will be performed by California Analytical Laboratories (CAL). Quality control (QC) analyses will be performed by the California Department of Food and Agriculture (CDFA) laboratory.

Results for soil analyses will be reported in ppm of carbofuran on a dry weight basis. Water samples will be analyzed for carbofuran with results reported in ppb.

Method Validation:

Seven replicate spiked samples at each of three concentrations will be analyzed for carbofuran in each matrix (water and soil). Water samples will be fortified at 10, 100 and 1500 ppb. Soil samples will be fortified at 0.1, 0.5 and 5 ppm.

Storage stability studies will be conducted for carbofuran in agricultural drain water and soil. Twenty soil samples will be fortified at 0.5 mg/kg. Twenty water samples will be fortified at 100 ug/L and acidified with sulfuric acid to pH 3. Duplicate samples will be analyzed after 0, 4, 7, 10 and 14 days for water and after 7, 14, 21, 28, 35, 42, 49, 56, 63, and 70 days for soil. The remaining 10 samples for water will be held in cold storage for analysis at additional intervals if deemed necessary due to extended storage times of field samples.

Continuing Quality Control:

One solvent blank, 2 distilled water spikes or 2 celite spikes (for soil), and 1 matrix spike will be analyzed with each set of samples except for background soils. Background soil samples will have 3 matrix spikes with each sample set rather than 1. Ten percent of all samples collected will be split and sent to the main laboratory (CAL) and the QC laboratory (CDFA) for analysis. The main laboratory will confirm 1 positive sample from each set of samples by a second method (high pressure liquid chromatography). For each confirmation, 2 replicate injections will be made for each analytical method. The QC laboratory will not confirm positives samples.

VII. TIMETABLE

Field site selection	March 12 - March 25
Sampling period	April - June 30
Chemical analysis	April - August 30
Statistical analysis	September 1 - November 30
Report preparation	December 1 - February 15
Final draft	March 15

VIII. BUDGET

Personnel		$ 25,000
Operating expenses		141,000
per diem	10,000	
vehicles	4,000	
materials	17,000	
laboratory	110,000	
TOTAL		$ 166,000

REFERENCES

1. Brian Finlayson, California Department of Fish and Game, Pesticide Investigations Unit. Personal communication to Jim Markle, FMC Corporation, October, 1987.

2. Ralph Shields, California Department of Food and Agriculture, Pesticide Enforcement Branch. Personal communication to Tom Anderson, Calif. Department of Food and Agriculture, August, 1987.