Study #108

California Department of Food and Agriculture (CDFA)
Environmental Monitoring and Pest Management
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PROTOCOL FOR ESTIMATION OF THE CONTRIBUTION FROM OFFSITE AERIAL DEPOSITION TO METHYL PARATHION RESIDUES IN AGRICULTURAL DRAINS IN THE SACRAMENTO VALLEY

I. INTRODUCTION

Recent environmental monitoring studies in the Sacramento Valley River Basin have raised concerns that observed levels of the organophosphate insecticide methyl parathion (MeP) in agricultural drainwater tributaries of the Sacramento River may contribute to invertebrate toxicity (DFG 1991; Foe and Conner 1991).

At issue is the source of this residual MeP and the identification of the most effective management practices to ameliorate the levels. MeP is a restricted use pesticide applied primarily for control of tadpole shrimp, leafhoppers, armyworms, cutworms, rice caseworms, rice bugs, and leaffolders in rice production. Residues in aquatic systems may be due to contributions from:

a) legal release after a specified holding period (3 days prior to 1991; expected to be 24 days during the 1991 season)
b) "other events" (e.g. early release, leaky drop boxes, etc.)
c) offsite aerial deposition during application
d) unapproved uses or uses incompatible with label (e.g. crayfish control)

This investigation will examine the effect of offsite aerial deposition and its contribution to the levels of MeP observed in agricultural drains that serve rice fields in the Sacramento Valley. No attempt will be made in this study to differentiate the components of offsite aerial deposition. Methyl paraoxon, the oxygen analog of methyl parathion, is a significant degradation product and its level will be measured for each sample along with MeP in this study.

II. OBJECTIVE

To determine the magnitude of MeP residues in agricultural drains as a result of offsite deposition during aerial application. From these data it will be possible to estimate the extent to which offsite aerial deposition is a factor in observed levels of MeP in aquatic systems.

III. PERSONNEL

Environmental Hazards Assessment Program personnel will conduct this study under the supervision of Randall Segawa, Senior Environmental Research Scientist. Other key personnel include:

Project Leader/Study Design/Data Analysis -	Judy Pino
Senior Staff Scientist -	John Troiano
Field Operations -	Bonnie Turner, Coordinator
	Rik Rasmussen, Lead
Lab Liaison/Quality Control -	Nancy Miller
Chemist -	Jane White
Agency and Public Contact -	Peter Stoddard (916-324-8916)

IV. EXPERIMENTAL DESIGN AND SAMPLING METHODS

Field Sites

Four agricultural drainwater ditches in Colusa and/or Glenn County that ultimately feed into the Sacramento River will be selected. One rice field served by each of the four drains will be monitored for MeP offsite aerial deposition during application.

The four rice field sites will be selected using the following criteria:

1) MeP will be aerially applied to the field.
2) No neighboring fields will be sprayed for MeP at the same time.
3) The field is physically adjacent to the drainage ditch.
4) The grower will cooperate and agrees to:
   a) allow automatic sampling equipment at sites above and below the field's outlet drain.
   b) allow mass deposition samples and meteorologic data to be obtained during MeP aerial application.

Advance notice of MeP spraying will be obtained from County Agriculture Department records and from direct reports by growers who have agreed to provide this information. MeP application rate will be determined from the grower/applicator records, but is anticipated to be at the label rate of 0.84 kg a.i./hectare of the 4E formulation (481 g a.i./L).

Two methods of sample collection and analysis will be used. On the banks of the ditch mass deposition cards will sample the aerial MeP deposition. Ditch water will also be sampled for the aqueous pesticide burden. It is anticipated that results of the two methods will agree well, and that the simpler MD card method will be shown to suffice. There is no report to date that demonstrates this, and both methods must be used for this study.

Aqueous Samples

Measuring stations will be established upstream and downstream from each selected field (see Site Diagram, page 11). The upstream site will be used to assess the background MeP level attributable to upstream sources; samples collected downstream from the field will be used to determine the contribution of offsite aerial deposition residues by correcting for the average [MeP] background measured upstream. A mesh screen will be set in the ditch to promote adequate aqueous mixing.

An Isco Model 2700 automatic sampling device will be used at the upstream and downstream stations to collect the composite samples. The samples will be collected in 1.8-L bottles on wet ice which contain sufficient HCl to adjust the sample to pH 3. The bottles will be capped with foil-lined lids, placed on wet ice and maintained at ~4 °C until their subsequent analysis. Samples will be analyzed for methyl parathion/paraoxon and the results will be corrected for extraction efficiency.

A. **Discussion:**

An order of magnitude estimate for the effects of offsite aerial deposition may be made as follows. The label application rate of 0.84 kg a.i./hectare corresponds to ~84 mg/m^2. For a drainage ditch with a square cross-sectional area of ~1 m^2 that borders a square 40-ha field, the area is ~636 m^2 and the volume is ~636 m^3. The mass deposition in

sampling variability. The first set will be collected after spraying has finished and when MeP is anticipated to be present at the sampling point; the second set will be collected immediately after the first. Each set will consist of four 1.8-L composite samples taken from points evenly spaced across the ditch transect. Each composite sample will consist of fifteen 120-mL subsamples hand collected at 1-minute intervals.

Mass Deposition Samples

Direct collection of MeP will be undertaken with mass deposition (MD) cards. These will consist of 0.09 m^2 plastic-covered cardboard squares mounted alongside the ditch. Just prior to spraying, absorbent Kimbie paper sheets will be affixed to the cardboard. Two hours after spraying has commenced (~90 minutes after completion), the MD cards will be collected and placed in 1-L amber glass bottles. They will be transported on dry ice and stored at -10 °C until analysis. Samples will be analyzed for methyl parathion/paraoxon and the results will be corrected for extraction efficiency.

Mass deposition will be analyzed at four locations: along the ditch adjacent to the field, within the field, and alongside the ditch in adjoining fields above and below the sample site. In addition, a field blank will be taken when the adjacent ditch samples are collected.

A. **Discussion:** The ***direct application*** scenario described for aqueous samples will deposit ~7.5 mg of MeP on a 0.09-m^2 MD card. The method validation for MD cards is currently being completed. However, if the limit of detection is 1 ppb, a lower limit of <0.1% of the direct application scenario should be detectable.

B. **Adjacent Samples:** Ten MD cards will be distributed along alternate sides of the drainwater ditch adjacent to the field under test. The five cards from each side of the ditch will be combined into two composite samples (inner bank and outer bank) and analyzed for methyl parathion/paraoxon.

C. **Neighboring Samples:** Four MD cards will be placed along the ditch both upstream and downstream from the test field, using the same spacing as for the adjacent samples. These will be combined into two composite samples (upstream and downstream) for analysis.

D. **Application Efficacy Field Samples:** Eight 0.09-m^2 mass deposition cards will be randomly placed in each field prior to spraying. These samples will be collected as described above and analyzed individually.

Meteorologic Measurements

A Met One weather station equipped with a CRI data logger will be used to record prevailing weather conditions including wind velocity and direction, ambient temperature, and relative humidity during MeP aerial application at the four sites.

Data Analysis

Samples are analyzed for methyl parathion and methyl paraoxon; the results are corrected for extraction efficiency. An estimate of the concentration and total mass of MeP likely to be found in the drainwater ditch contributed by offsite aerial deposition may be obtained as follows:

-A background MeP concentration is established from the mean of the eight individual upstream composite samples. Each of the eight individual downstream composite samples is corrected for this background to yield a time series of MeP offsite aerial deposition estimates.

-The volume of water passing by the downstream collection point during the collection period is:

~(ditch cross-sectional area) x (flow rate) x (collection time)

The mass of MeP resulting from offsite aerial deposition is the product of the average MeP concentration of the eight composite samples collected downstream and the volume of water passing by that collection point.

The values for mass deposition from analyses of the drainwater samples will be compared to the results from the composite mass deposition cards placed along

the ditch. Good correlation between these may justify use of the cards as an effective single technique for estimating offsite aerial deposition.

Constraints

A. **Flow Rate:** If the drainage ditch flow rate is inadequate due to the drought situation or very conservative water management practices, aqueous samples will not be collected. In this case, the concentration and mass deposition in the ditch may be estimated using results from the mass deposition cards.

B. **Confounding Factors:** No attempt will be made in this study to differentiate or to quantify the effects of variables on the magnitude of offsite aerial deposition including: drift and swath displacement; wind speed, direction, and turbulence; ambient temperature and RH; spray droplet size; plane's altitude and speed; etc.

C. **Regional Interpretation:** The ultimate contribution of drainwater MeP to levels in major waterways depends on flow patterns in tributary systems that are beyond the scope of this study. If the levels observed in this study appear to warrant further investigation, new studies will be required that control for confounding factors.

V. CHEMISTRY METHODS AND QUALITY CONTROL

Each of the 197 samples (133 aqueous and 64 mass deposition - see Section VII, page 8) will be analyzed for methyl parathion/paraoxon by FPD gas chromatography at the California Department of Food and Agriculture Chemistry Laboratory Services Branch (CDFA). One matrix blank and one matrix spike will be analyzed with each extraction set of (~10) samples; the concentration of the matrix spike will be rotated through the linearity levels for each matrix, and will also depend on anticipated field sample concentrations.

Duplicate analyses of 10% of the aqueous samples will be provided by the main lab (CDFA) and by the QC lab (Enseco Laboratory, West Sacramento, CA). The result reported for each sample will be corrected for the extraction efficiency of the method.

VI. TIMETABLE

Field site selection:	March - April 1991
Field sampling period:	April - May
Chemical analyses:	June - July
Data analysis:	August - September
Report preparation:	October - November
Final draft:	December

VII. ESTIMATED NUMBER OF SAMPLES FOR CHEMICAL ANALYSIS

	Aqueous		Mass Deposition		Total
	Upstream	Downstream	Ditch	Field	
For 1 Site:					
Background:	8				8
Offsite Aerial Deposition:		8	4		12
Sampling Variability:		8			8
Application Efficacy:				8	8
Field Blanks		1	1		2
Subtotals:	8	17	5	8	38
For 4 Sites:	32	68	20	32	160
+ 10% split samples	4	7			11
+ 10% matrix spikes	4	7	2	4	17
+ 10% matrix blanks	4	7	2	4	17
	44	89	24	40	
Totals	133		64		197

VIII. BUDGET

Personnel			$16,200
Operating Expenses			
per diem	($1,260/site x 4 sites)	5,040	
vehicles	($600/site x 4 sites)	2,400	
materials	(bottles, gloves, etc.)	5,000	
laboratory	($150/sample x 197 samples)	29,550	41,990
TOTAL			**$58,190**

IX. REFERENCES

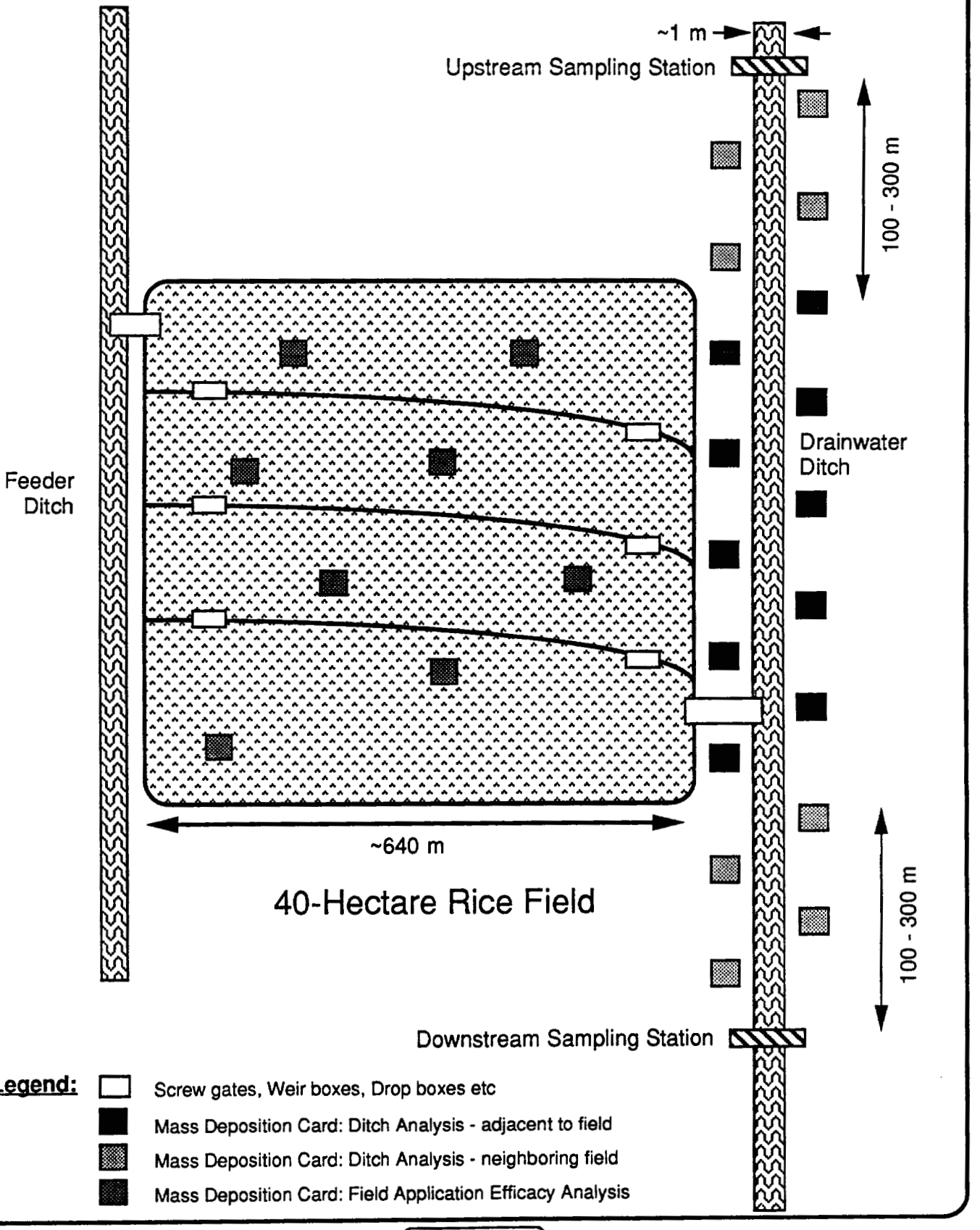
Cheminova, Ltd. 1985-90. Data submitted to CDFA's Registration Branch, Registration Package Nos. 121-033, -052, -058, -059, -080.

DFG 1991 (unpublished). Toxicity of Colusa Basin Drain Water to Young Mysids and Striped Bass, 1990. Department of Fish and Game, Sacramento, CA.

Foe, C., and V. Connor. 1989. 1989 Rice season toxicity monitoring results. Staff memorandum California Central Valley Regional Water Quality Control Board, Sacramento, California.

Methyl Parathion Offsite Deposition Study

Site Diagram



J.A.Pino 25-feb-91