#107

California Department of Food and Agriculture
Environmental Monitoring and Pest Management
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PROTOCOL TO SAMPLE METHYL PARATHION AND METHYL PARAOXON IN PADDY WATER OF COMMERCIAL RICE FIELDS

I. Introduction

Methyl parathion (*o*,*o*-dimethyl *o*-4-nitrophenyl phosphorothioate) is an organophosphate insecticide and acaricide used to control tadpole shrimp (*Triops longicaudatus*) in California rice fields. In 1988, more than 32,900 pounds were applied in the rice-growing region of Colusa county.

Methyl parathion has been detected in Colusa Basin Drain water samples at levels that impact aquatic organisms. Concentrations found during May of 1990 ranged from 0.12 to 0.66 µg/L (Central Valley Regional Water Quality Control Board, 1989; Department of Fish and Game, 1990). Pursuant to the amendment of the Water Quality Control Plan for the Sacramento River, Sacramento-San Joaquin Delta and San Joaquin basins (Central Valley Regional Water Quality Control Board Resolution No. 90-028), water management practices that reduce methyl parathion concentrations in surface water must be implemented. For 1991, such practices must meet a 0.26 µg/L performance goal (daily maximum) in all waters designated as freshwater habitat. Approved water management practices following methyl parathion applications to rice prohibit the discharge of irrigation water from rice fields until the 25th day following application (California State Water Resources Control Board, 1991). Additional field dissipation data is needed to assess the adequacy of this mitigation measure.

In soil and aquatic systems, methyl parathion may be degraded by metabolic conversion to methyl paraoxon, hydrolysis to *p*-nitrophenol and dimethyl-*o*-thiophosphoric acid or nitro-group reduction to methyl aminoparathion (Eichelberger & Lichtenberg, 1971; Sharmila et al., 1988).

Under flooded soil conditions, it has been shown that the major route of degradation is through the latter mechanism because the predominately anaerobic conditions favor reduction by surface attached and sediment bacterial populations (Badawy & El-Dib, 1984; Crossland & Bennet, 1984; Crossland et al., 1986; Sharmila et al., 1988). Hydrolysis by bacterial populations suspended in the water column is a minor degradation pathway. The decline of methyl parathion in aquatic or flooded soil systems has been shown to be first order (Badawy & El-Dib, 1984; Sabharwal & Belsare, 1986; Seiber & McChesney, 1987). Half-lives reported in the literature are listed below:

Half-life, days	Reference	Conditions
1.8	Seiber & McChesney, 1987	1
3.25	Dortland, 1980	2
4.13	Dortland, 1980	3
5.17	Sharmila et al., 1988	4
5.68	Sabharwal & Belsare, 1986	5
5.96	Crossland et al., 1986	6
8.75-17.08	Crossland & Bennet, 1984	7
9.9	Stephenson & Kane, 1984	8
11.9	Stephenson & Kane, 1984	9
13.3	Stephenson & Kane, 1984	10
15.7	Badawy & El-Dib, 1984	11
23.1	Badawy & El-Dib, 1984	12
35.3	Cheminova, 1988	13
44.6	Cheminova, 1988	14

1. Flooded rice field, pH 7, 27°C.
2. Aquaria (water, sediment, aquatic vegetation), pH 7.4.
3. Aquaria (water, sediment, aquatic vegetation), pH 7.7.
4. Laboratory incubation study using flooded alluvial soil, 25°C.
5. Carp rearing pond (water, sediment, aquatic vegetation).
6. Outdoor pond
7. Outdoor pond, pH 7.7-10.3, 10-17°C.
8. Outdoor ponds, pH 9-10.8.
9. Outdoor ponds, pH 8.7-11.3.
10. Outdoor ponds, pH 8.8-11.1.
11. Freshwater, pH 8.5.
12. Brackish water, pH 8.5.
13. Distilled water, 25°C, pH 7.
14. Distilled water, 25°C, pH 9.

II. Objective

The objective of this study is to quantify concentrations of methyl parathion and methyl paraoxon found in paddy water from commercial rice fields in Colusa county over time, and calculate the dissipation half-life in each field.

III. Personnel

This study will be conducted by Environmental Hazard Assessment Program personnel under the overall supervision of Randall T. Segawa, Senior Environmental Research Scientist.

Project Leader: Wynetta Kollman
Senior Staff Scientist: Lisa Ross
Field Operations: Bonnie Turner - Coordinator
Pam Wofford - Lead
Primary Laboratory: CDFA Chemistry Lab Services, Meadowview
Jane White - Chemist
Quality Control Laboratory: California Analytical Lab, W. Sacramento
Laboratory Liaison/Quality Control: Nancy Miller
Agency/Public Contact: Peter Stoddard [(916) 324-8916]

IV. Experimental Design

Field Sites

Four commercial rice fields in Colusa county will be selected based on similarity in cultural and water management practices used and growers' permission for field access. Selection will be made from the population of fields with a 24-day holding time for methyl parathion. Methyl parathion applications to rice are usually made by air at a recommended label rate of 0.70 Kg a.i./hectare (1 pint formulated product/acre). In this study, application efficiency will be estimated in the bottom paddy of each field by measuring the mass deposited during application on eight randomly located 0.09 m^2 polyethylene-backed absorbent paper sheets pinned to platforms parallel to and 1 ft. above the water surface.

Sampling

Two composite water samples will be collected from the bottom paddy of each field. A composite sample will consist of 4 randomly collected subsamples. Water samples will be collected at -1 (background), 0, 1, 2, 4, 6, 8, 12, 16, 20 and 24 days after application. On each sampling day, the following measurements will be made at random in the bottom paddy of each field:

1. Water depth (in centimeters) at 6 to 10 locations.
2. Water temperature at 4 locations.
3. Water pH at 4 locations.

Data Analysis

Regression analyses using the SAS General Linear Models procedure will be conducted to relate methyl parathion and methyl paraoxon concentrations in paddy water with day after application.

V. Sampling Methods

Water samples will be collected from the bank of the bottom paddy with an open glass quart jar attached to an extension pole, composited in a one liter amber glass bottle and acidified to pH 3 with concentrated hydrochloric acid. Sample bottles will be sealed with Teflon®- lined caps and placed immediately on wet ice; samples will be stored at 4°C until analyzed.

VI. Analytical Methods/Quality Control

Method Validation

An analytical method has been developed for the determination of methyl parathion in water in prior studies. Results of the analyses will be reported in ppb. Method validation for the determination of methyl paraoxon in water and on polyethylene-backed absorbent paper sheets will be conducted by the primary laboratory. Three replicate analyses at three different spike levels will be used to determine the accuracy (based on the mean percent recovery) and precision (based on the standard deviation) of each method.

Storage Stability

The determination of methyl parathion storage stability will be conducted under a different study. Two replicate water samples will be spiked with 5 ppm methyl parathion, acidified to pH 3 and stored at 4°C. Samples will be analyzed after 0, 14, 28, 42 and 56 days.

Continuing Quality Control

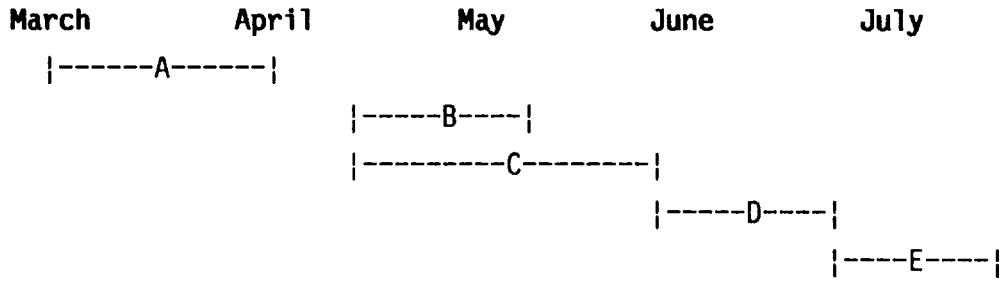
The following analyses for methyl parathion and methyl paraoxon will be conducted by the primary laboratory for continuing quality control. An extraction set will consist of 8-20 samples:

1. Solvent blanks - one for each extraction set to detect any laboratory contamination.
2. Blank-matrix spikes - one for each extraction set to check the accuracy and precision of the analytical method.
3. Split matrix samples - For a qualitative and quantitative check of the primary method, randomly collected samples (10% of the paddy water samples) will be split into two aliquots, one aliquot analyzed by the primary laboratory and one aliquot to be analyzed by the quality control laboratory. Split matrix samples will be collected on days 0, 2 and 12 after application.

The approximate number of samples to be analyzed by the primary laboratory is 180:

Field samples		
Rice paddy water ([11 samples x 2 reps] x 4 fields)	=	88
Appl. efficiency (8 samples x 4 fields)	=	32
Method Validation		
Oxygen analog, water (3 spikes x 3 reps)	=	9
Oxygen analog, paper sheets (3 spikes x 3 reps)	=	9
Storage Stability (Analyses done under a different study)	=	0
Continuing Quality Control		
Solvent blanks (1 x 15 extr. sets)	=	15
Blank-matrix spikes (1 x 15 extr. sets)	=	15
Split matrix samples	=	12
TOTAL		180

VII. Timetable



A. Field sites selection
B. Sampling period
C. Chemical analyses
D. Data analysis
E. Final report

VIII. References

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Study 107
Methyl Parathion
Field Dissipation

Revised Sampling Plan

Take water samples on the following days after application:

2	3	4	5	7	9	11	15	19	23
*		*		*		*			

Total number of samples is 92:

Rice paddy water ([10 samples x 2 reps] x 4 fields)	=	80
Split matrix samples	=	12
TOTAL		92

a. A split sample will be taken on the starred days.
b. Application efficiency will not be included in the study.