Protocol for Environmental Hazards Assessment
Program (EHAP) Rice Herbicide Monitoring Project

I Objectives

A. To characterize the dynamics of rice herbicides in the field (mass balance).
B. Characterize the water flow dynamics of herbicide laden water from fields.

II Personnel

The monitoring of the Environmental fate of rice herbicides will be conducted by personnel in EHAP under the overall supervision of Ronald J. Oshima. All inquiries regarding the progress and/or results of any facet of the monitoring program should be directed to Ron Oshima in Sacramento (phone 916-322-2395 or ATSS 492-2395).

Tom Mischke - Responsible for selection of sampling methodology and liaison to CDFA Chemistry Laboratory Services. Questions concerning all aspects of the chemical analysis of collected samples should be directed to him (phone 916-322-2395 or ATSS 492-2395).
Field sampling, establishing sample locations, and liaison with county officials, growers, and other state agencies will be the responsibility of Joe Franz and Roger Sava. Questions concerning these aspects of the study should be directed to them (phone 916-322-2395 or ATSS 492-2395).

Cooperating Agencies

1. State Department Water Resources, Northern district will construct and maintain water metering devices on two fields and supply daily water flow readings.
2. Colusa and Glenn County Agricultural Commissioner's staff may assist in locating co-operative growers and supplying pesticide application records.
3. State Water Resources Control Board (SWRCB) will review this protocol for design approval.

III Study Timetable

Field monitoring will begin with the first applications of herbicides to test fields. The duration of the study will be approximately 32 days after the final application of herbicides to these fields.
**IV General Monitoring Plan**

**Section 1**
The study design will be separated into three sections. The first section will deal with the intensive monitoring of two rice fields to determine the amount of rice herbicides impacting the field, mobility of the material within the field, degradation of parent compound and amounts leaving the field via overflow or volatilization. In addition, the field dynamics of water flow into and out of the field as well as loss of water due to evapotranspiration will be determined.

**Section 2**
The second section will involve the collection of samples from a maximum of twenty rice fields over a sixty day period. These samples will provide information on concentration of herbicide vs flow of water. These data points will then be used in conjunction with a statistical model to predict field water flows.

**Section 3**
Development of a statistical water flow model from data obtained from Section 1. This model will be utilized...
to predict flows from the fields in the water flow
dynamics section of this study.

V Sampling Design and Monitoring Timetable

A. Mass Balance Section

1. Water, Vegetation & Sediment Sampling
   a. Site Location:
      Two fields will be selected for the mass
      balance section of this study.

      Within each field, four paddies stratified
      throughout the field will be selected for
      sampling. Four sampling locations will be
      selected within each of these four paddies, and
      will be arranged as in Figure 1. These
      locations will be located approximately ten
      feet from the inlet, ten feet from the bank and
      ten feet from the outlet.

      Figure 1.
b. Sample Collection:
Water, vegetation, and sediment samples will be collected from all sampling locations (16) in a field. At time of collection, a sampling cylinder will be depressed into the sediment at the collection site. The water volume contained within the confines of the cylinder walls will then be transferred using a hand pump and hose into one liter amber bottles.

After the removal of the water, any vegetation will be collected and placed into a five hundred ml amber bottle. The remaining top two inches of sediment will then be removed and placed into a separate five hundred ml amber bottle.

In addition to the sixteen field sites, replicate water samples will be obtained from the inlet and outlet of the field. These samples will be obtained using one liter amber bottles.

c. Sampling Timetable
A water, and sediment sample will be collected at each of the above sites prior to the first
application of ordram. Water, vegetation and sediment samples will be collected at each of these sites during the day of application and post spray days 2, 4, 8, 16, and ending on day 32. If a second application of ordram or bolero is applied during this 32 day period, the sampling scheme will revert back to the original timetable and an additional background sample will be taken. The sampling will then end on the 32nd day after the final application of herbicide to the field.

2. Air Sampling

Three hour air samples will be collected to determine the quantity of bolero, ordram and MCPA volatilizing off of the study field. These samples will be obtained using hi volume air samplers. These samplers will be located along the perimeter of the field, with the air samples being collected from the north, south, west and east borders of the field. The sampling scheme will consist of four sampling days, 0, 1, 2, and 6 with day 0 being the background.
3. Mass Deposition

Adjacent to each of the water sampling sites, a cone sampler with a 1 ft$^2$ opening will be employed to measure mass deposition during the aerial application of ordram and bolero. During the application of MCPA a one ft$^2$ polyethylene backed absorbant paper will be employed at each of these above sites.

4. Field Dynamics

Department of Water Resources will provide information on flow into and out of the two study fields as well as the evapotransporation for each of these fields. During collection of water samples, water depth and ambient water temperature will be recorded. In addition, on site weather stations will record ambient air temp, humidity, wind speed and wind direction.

5. Tank Samples

Tank samples will be collected prior to the application of ordram, bolero and MCPA prior to the application. Sample will be collected in a 500 ml amber jar.
B. Water Flow Dynamics Section

1. Site Locations
   A maximum of 20 rice fields will be chosen as sampling sites. Fields will be chosen based on: location within the study area, ability to measure water flow into and out of fields, cooperation of growers and accessibility to these fields.

2. Flow Dynamics
   Estimation of field flows with a statistical model from the mass balance study will be attempted.

   Flow measurements will be taken 1 or 2 times per day every 3rd day for a 30 day period for each field. In addition, temperature and humidity measurements will be taken coincidentally with flow sampling to provide a data base characterizing flow variation due to weather changes. Although the model will be unable to predict flow variation due to an irrigation manipulation of rice boxes, it is hoped that a record of major changes might be obtained from cooperative irrigators.
3. Water Sampling

Water samples will be taken from the inlet and from the point where the last paddy drains from the field. Samples from each of these two sites will be collected using one liter amber bottles sealed with foil.

4. Sampling Timetable

Monitoring schedule for each of these fields will begin the day flooding is completed. Samples will be taken every third day for a period of time dependent on the final application of herbicide to a particular field. Accompanying each water sample, information will be recorded at each sample site to tabulate information on ambient air temp., humidity, water temp. of paddy, and depth of water at sampling point at time of sampling.

5. Handling and Storage of Samples

All sampling media and containers will be prepared and pre-numbered at the California Department of Food and Agriculture Laboratories in Sacramento. Each device or container will
be shipped to the sampling sites with an accompanying Chain of Custody Record. The Chain of Custody Record will be filled out by all parties handling or storing the sampling media or sample containers from the time they leave the Sacramento CDFA lab until they are returned to the lab for analysis. The Chain of Custody Record also contains an internal chain of custody record for use by the laboratory.

All samples will be collected by EHAP personnel, sealed in glass containers and stored in the following manner until and during transport to the CDFA laboratory in Sacramento.

**On Dry Ice (-70°C)**
- Mass Deposition
- Air Samples
- Sediment

**On Ice (4°C)**
- Water Samples
- Vegetation Samples
- Tank
6. Analysis of Samples
All samples will be analyzed by CDFA Chemistry Laboratory Services in Sacramento. Quality control duplicate samples will be analyzed by CDFA and another approved laboratory. Approximately 1-2% percent of the total number of each type of sample collected will have duplicate analysis performed as part of the quality control program. Brief details of the analytical methods for each type of sample are available if requested.
Water

Background \[(2\text{Fields})(16\text{ Sites})(1\text{ Day}) + (2\text{ Sites})(2\text{ Rep.})(1\text{ Day})(2\text{ Fields})\] \[\times 3\text{ Chemicals} = 120\]

Bolero (1 Field)(16 Sites)(6 Days) + (1 Field)(2 Sites)(6 Days)(2 Reps.) = 120


MCPA (2 Fields)(16 Sites)(6 Days) + (2 Fields)(2 Sites)(6 Days)(2 Reps.) = 240

Water \[720\]

Vegetation

No Ordram Background

Ordram (2Fields)(16 Sites)(6 Days) = 192

Bolero Background (1 Field)(16 Sites)(1 Day) = 16

Bolero (1 Field)(16 Sites)(6 Days) = 96

MCPA Background (2 Fields)(16 Sites)(1 Day) = 32

MCPA (2 Fields)(16 Sites)(6 Days) = 192

Total \[528\]

Sediment

Ordram Background (2 Fields)(16 Sites)(1 Day) = 32

Ordram (2 Fields)(16 Sites)(6 Days) = 192

Bolero Background (1 Field)(16 Sites)(1 Day) = 16

Bolero (1 Field)(16 Sites)(6 Days) = 96

MCPA Background (2 Fields)(16 Sites)(1 Day) = 32

MCPA (2 Fields)(16 Sites)(6 Days) = 192

Total \[560\]
Air
Bolero (1 Field)(4 Samples)(4 Days) = 16 samples
Ordram (2 Fields)(4 Samples)(4 Days) = 32 samples
MCPA (2 Fields)(4 Samples)(4 Days) = 32 samples

Teflon Box Deposition
Bolero (1 Field)(16 Sites)(2 Applications) = 16 fallout box
Ordram (2 Fields)(16 Sites)(1 Application) = 32 fallout box

Fallout Deposition
MCPA (2 Fields)(10 Sites)(1 Application) = 32 fallout sheets

Tank
Ordram (2 Fields)(1 Application) = 2
MCPA (2 Fields)(1 Application) = 2
Bolero (1 Field)(1 Application) = 1

Flow Dynamics Water Samples
All herbicides (20 Fields)(2 Sites)(20 Days) = 800 water samples

Total # of water
- vegetative: 528
- sediment: 560
- air: 80
- teflon box: 48
- fall out: 32
- tank: 5

Mass Balance Total: 1973
Flow Dynamics Total: 800

\[ \text{Total} = 2773 \]