CALIFORNIA DEPARTMENT OF PESTICIDE REGULATION (DPR)
Environmental Hazards Assessment Program (EHAP)

Laboratory Project Plan and Protocol for the 2002 Rice Pesticides Monitoring Program
Study #206
March 18, 2002

Organization and Responsibility

KayLynn Newhart is the project leader, agency contact person, and EHAP laboratory liaison for DPR's Rice Pesticide Program. The duties associated with the program include: Reviews laboratory QA/QC plans and QA reports; meets or communicates with field sampling consultant and sample custodian to evaluate progress and resolve problems; reviews and maintains QA reports.

All laboratories should report all analytical data and information to KayLynn Newhart at (916) 324-4190, knewhart@cdpr.ca.gov.

Protocol

The monitoring program shall follow the approved written EHAP protocol. Changes to the protocol must be approved by the EHAP.

Quality Assurance Objectives

Each laboratory will use their method detection limit (MDL), instrument detection limit (IDL) and a reporting limit (RL) for each analyte as documented in their analytical methods agreed between each analytical laboratory and DPR.

Method Validation

The mean and standard deviation (s) values from the method validation studies will be used to set warning and control limits at +\-2s and +\-3s, respectively. **Each laboratory will be required to notify the EHAP laboratory liaison of any changes or procedures made to their analytical method before analyzing any field samples.**

Continuing Quality Control

Accuracy is defined as a determination of how close the measurement is to the true value and is often described as percent recovery. Accuracy is to be expressed as Percent Recovery (%). All calculated values for accuracy shall be presented with the analytical results. The equation for calculating Percent Recovery is as follows:

$$\text{Percent Recovery (\%)} = \frac{\text{sample concentration}}{\text{matrix spike concentration}} \text{ X } 100$$

Accuracy will be assessed by requiring each laboratory to analyze **two** matrix spike samples per analyte for each extraction set of up to twelve field samples (Appendix 1).

Accuracy control charts will be plotted by EHAP for each chemical and method and for each control sample matrix. The warning and control limits are established as listed in the method validation section. If any continuing quality control spike recovery is not within the limits of these criteria, the following is required:

1. A check shall be made to be sure there are no errors in calculations, surrogate solutions, and internal standards. A check shall also be made on instrument performance.

2. All affected data shall be recalculated and/or the extract shall be reanalyzed if any of the above checks reveals a problem.

3. All affected samples shall be re-extracted and reanalyzed if none of the above is identified as a problem.

4. All analytical data shall be flagged as suspect if the accuracy still does not fall within the limits of the above criteria. The laboratory QA officer shall notify the EHAP QA officer within one working day after discovery of suspect data.

5. If an unacceptable value cannot be corrected, additional samples may be analyzed to determine the validity of the original sample results.

The calibration curve should be prepared such that one standard is at the reporting limit and one is higher than the highest expected amount. If after initially shooting the sample extract the concentration of the analyte falls outside the calibration range, the sample should be diluted so it falls within the calibration range. **Each laboratory shall notify the EHAP laboratory liaison of any changes in their calibration procedures.** As an interlaboratory quality control check a minimum of ten percent of the total samples collected may be analyzed by a second laboratory for verification. California Department of Food and Agriculture Center for Analytical Chemistry (CDFA) laboratory will analyze split samples for molinate, thiobencarb and primary analyses for

methyl parathion, and malathion. Quality control analyses for methyl parathion and malathion will be performed by California Department of Fish and Game Water Pollution Control Laboratory (DFG). Primary sample analyses for molinate will be performed by Syngenta, registrant for Ordram®. Primary sample analyses for thiobencarb will be performed by Valent Dublin Laboratory, registrant for Bolero® and Abolish®.

In addition, rinse blank samples for each chemical will be collected from CBD5 during weeks 4 and 8 to check for potential field contamination. Blind matrix samples will be routinely submitted to each laboratory to check for accuracy.

Background surface water will be provided by EHAP to the laboratories and used for control and fortification samples.

Backup field samples collected and stored during the study may be analyzed if sample breakage occurs or if sample results between the primary and quality control laboratories are dissimilar.

Audits of the field sampling and lab analysis may be conducted.

Reporting

Results of field sample and continuing quality control analyses shall be reported to the EHAP laboratory liaison within **21 days of the date samples are received at each laboratory**. Each laboratory shall submit legible, organized reports that contain analytical results of all samples received from EHAP. **Analytical results are to be expressed as ppb for all samples to three significant figures.** Positive matrix blank results shall be reported. Do not correct field sample results for background levels. Indicate if the results have been adjusted for spike recoveries. **Each laboratory shall notify the EHAP laboratory liaison of any changes in their procedures for reporting sample results including number rounding procedures.** The report shall evaluate the quality of the individual sample data, based on the method validation analyses. The reports shall include the following:

1. Chain of custody (COC) forms; all analytical results are to be reported on the COC, including the name of the person extracting and analyzing the sample, date of extraction and the date of analysis for each sample.
2. Records of any quality assurance problems and questions pertaining to the samples analyzed.
3. Calculations of accuracy.
4. Reporting Limit (RL); for those samples that contain no detectable amount, write ND and indicate the RL.
5. Case narrative, if the data requires it.

In addition, the laboratory shall be prepared to provide to the EHAP lab liaison all sample custody paperwork, records of times and dates of analyses, and raw data pertaining to both the analyses and the quality control checks within 10 working days after the information is requested.

Archives

All backup samples and sample extracts shall be stored frozen or refrigerated until EHAP authorizes their disposal.

All raw data, including chromatograms, memoranda, notes, worksheets, and calculations that are necessary for the reconstruction and evaluation of the study shall be archived at each respective laboratory for at least three years.

2002 Rice Pesticide Continuing Quality Control Procedures

Using background surface water, each laboratory will generate and analyze the following blank matrix and matrix spikes with each extraction set in order to determine accuracy over the duration of the study. All continuing quality control data will be submitted to the EHAP laboratory liaison **with each extraction set**. Make sure individual field sample numbers are clearly identified with each set.

Methyl Parathion and Malathion	CDFA	DFG
1 blank and **2** matrix spikes	0.2 ppb	0.2 ppb
Molinate	Syngenta	CDFA
1 blank and **2** matrix spikes	5.0 ppb	5.0 ppb
Thiobencarb	Valent	CDFA
1 blank and **2** matrix spikes	1.0 ppb	1.0 ppb