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Department of Pesticide Regulation  
Division of Pest Management, Environmental Monitoring, Enforcement, and Licensing  
Environmental Monitoring Branch  
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STUDY NUMBER 211: MONITORING METHYL PARATHION AIR  
CONCENTRATIONS ADJACENT TO AN ORCHARD APPLICATION

June 2002

**I. INTRODUCTION**

The Department of Pesticide Regulation (DPR) is responsible for evaluating pesticide compounds to determine whether certain active ingredients pose a potential threat to public health as toxic air contaminants (TAC). In 1986, at the request of DPR, Air Resources Board (ARB) staff measured methyl parathion air concentrations in the residential areas of Sutter and Colusa Counties. Results from collected air samples indicated that persons residing near agricultural applications were potentially exposed to methyl parathion via the inhalation route when flooded rice fields were aeriually treated during the peak use months of May and June (ARB, 1986). Based on review of the ARB study, in addition to review of other published methyl parathion studies, DPR determined that methyl parathion poses a present or potential hazard to human health and designated it a TAC in 2000. Once a pesticide compound has been evaluated and identified as a TAC, DPR must then determine adequate control measures to reduce public exposure to the compound (DPR, 2001).

Methyl parathion (O,O-dimethyl O-p-nitrophenyl phosphorothioate) is an organophosphate pesticide with insecticidal and acaricidal activity. It is a nonsystemic compound that controls sucking and biting pests by contact, stomach, and respiratory action. This compound is classified as a Restricted Use Pesticide because of its acute toxicity towards humans and birds. Because it is a cholinesterase inhibitor, acetylcholine, a synaptal neurotransmitter, may accumulate in such abundance that it interferes with the neuromuscular junction, resulting in twitching episodes in acutely toxic situations (Ware, 1983). Methyl parathion degradation in the environment may result in its conversion to methyl paraoxon, the more toxic oxygen analog. These reactions have been observed to occur in light, water, soil, and air (DPR, 1999).

Currently, Penncap-M<sup>®</sup> is the only methyl parathion product available. It is flowable formulation consisting of polymeric microcapsules designed for slow release of methyl parathion. In 2000, there were two additional methyl parathion products available in California, however, registration for these two emulsifiable concentrate formulations are no longer presently active.

In January 2000, the US Environmental Protection Agency (USEPA) cancelled methyl parathion use in all fruit and some vegetables crops, citing that the pesticide posed an unacceptable dietary risk to the young (USEPA, 1999). Among the crops cancelled were apples, peaches, pears, grapes, nectarines, cherries, plums, tomatoes, carrots, artichokes, broccoli, Brussels sprouts, cauliflower, celery, collards, kale, kohlrabi, lettuce, mustard greens, rutabagas, spinach, turnips, and fresh peas and beans. Pesticide usage was also cancelled for nonfood crops such as ornamentals, grasses grown for seed, mosquito use, and nursery stock.

Because of these new restrictions, methyl parathion use within several California counties (Table 1) was abruptly reduced in the year 2000 (Table 1), as many of the prior applications were directed to tree or other food crops (Table 2). Use on walnuts, however, was unaffected in 2000 and data indicate (Table 2) that methyl parathion use appears to be increasing for that crop.

Table 1. Ten California counties with highest total methyl parathion use from 1996-2000

County	Pounds of Active Ingredient Used by Year					Total
	1996	1997	1998	1999	2000	
Tulare	24,875	26,991	25,285	26,093	32,931	136,176
San Joaquin	9,883	20,362	30,942	31,315	16,841	109,344
Fresno	23,634	21,025	21,605	19,212	811	86,288
Sutter	14,610	15,766	6,177	14,772	3,551	54,877
Sacramento	9,010	6,010	16,149	10,533	5	41,708
Contra Costa	5,363	3,644	12,227	10,206	3,157	34,598
Stanislaus	1,970	4,249	4,763	11,958	9,890	32,830
Kern	2,929	18,422	7,151	3,940	317	32,759
Yuba	9,973	8,287	5,056	5,394	1,700	30,411
Lake	2,801	4,777	12,194	5,603	0	25,376

Information obtained from DPR pesticide use database

Table 2. Ten crops with highest total methyl parathion use from 1996-2000

Crop	Pounds of Active Ingredient Used by Year					Total
	1996	1997	1998	1999	2000	
Walnut	0	15,215	34,391	59,802	72,869	182,277
Peach	30,240	33,822	12,790	22,828	44	99,724
Pear	13,708	13,862	36,559	21,722	40	85,891
Plum	17,513	16,191	15,799	10,190	13	59,707
Apple	7,656	18,653	18,816	13,309	10	58,444
Nectarine	15,707	13,579	12,780	12,790	31	54,887
Grapes	7,129	19,891	9,646	1,731	0	38,396
Corn (as food)	5,044	5,569	10,238	9,662	4,651	35,164
Alfalfa	12,470	7,990	5,353	3,327	12	29,153
Onion (dry)	1,139	1,619	802	1,075	254	4,889

Information obtained from DPR pesticide use database

Traditionally, methyl parathion is applied to walnut orchards by ground or air to control the codling moth (*Cydia pomonella*) that can cause damage to the developing nut crop from May to August in the San Joaquin Valley. With repeated applications, this compound is very effective in reducing the pest population resistant to organophosphate and/or pyrethroid insecticides. PennCap-M<sup>®</sup> Special Local Need (SLN) Label information indicates that the maximum application rate to walnuts is 2 pounds active ingredient/acre with a minimum spray interval of 21 days between applications (DPR 2000).

To protect public health from exposure to fumigants, DPR staff use a computer modeling program (USEPA's ISCST3 - Industrial Source Complex-Short Term Model:Version 3) to determine the volatilization rate into the atmosphere from different types of applications (Johnson et. al, 1999). This model has served as a useful tool and has allowed staff to establish restrictions to protect those who work or reside near field applications of fumigants. Consequently, these restrictions reduce public exposure to the compound and also allow for continued use of the agricultural product. One of the desires of this current study is to determine the adequacy of the ISCST3 model for use with a nonfumigant compound in an orchard setting, which contrasts with the open field settings that have been simulated for field fumigants.

## **II. OBJECTIVE**

The study objectives are 1) to measure methyl parathion and its breakdown product, methyl paraoxon in air concentrations in association with a field application, 2) to determine if the USEPA's ISCST3 model is an appropriate theoretical model to use for the interpolation/extrapolation of methyl parathion air concentration data and, 3) to document the expenditures and resources needed to successfully conduct this type of air monitoring study.

## **III. PERSONNEL**

This study will be conducted by personnel from the Environmental Monitoring Branch under the overall supervision of Randy Segawa, Senior Environmental Research Scientist. Personnel responsibilities are listed in SOP ADMN002.00. The key personnel include:

Project Leader	Clarice Ando
Senior Staff Scientist	Bruce Johnson
Field Coordinator	Pam Wofford
Assistant Field Coordinator	Suzanne Matsumoto
Statistician/Modeler	Bruce Johnson
Laboratory Liaison	Carissa Ganapathy
Analyzing Laboratory	California Department of Food and Agriculture, Center for Analytical Chemistry
Agency and Public Contact	Randy Segawa

All questions concerning this project should be directed to Randy Segawa at (916) 324-4137 or to the e-mail address RSegawa@cdpr.ca.gov.

#### **IV. STUDY DESIGN**

##### General Sampling Plan

In conjunction with the county agricultural commissioner's staff, we would like to ideally locate a study area which meets the following criteria 1) a walnut orchard 10 to 40 acres in size, 2) no tall crops, buildings, or other obstructions which would interfere with air flow movement patterns within 500 feet on all sides of the walnut orchard perimeter, 3) maximum label rate of two pounds active ingredient/acre applied by ground or air to the orchard, 4) application should be completed within the same day as started and, 4) should have full cooperation from the walnut orchard owner and all surrounding land owners so that monitoring equipment may be placed around the orchard perimeter and remain undisturbed for a five consecutive day period.

To complete this study, from one to three methyl parathion applications will be monitored.

##### Design

Once a monitoring site is selected, 16 low volume air samplers will be stationed around the study field in a circular pattern: two concentric circles, each composed of 8 low volume air samplers will be positioned around the study site at 30 and 150 feet distances from the field edge prior to pesticide application (Figure 1).

Air samples will be collected at three sampling intervals: a background period sample, an application period sample, and a post application period sample. For the background period sample, a single air sample will be collected over a 12-hr duration from one of the 16 low volume air samplers stationed around the field perimeter. This sample will originate from the air sampler located in the prevalent downwind direction with relationship to the field location. Prevailing wind direction will be determined by previewing meteorological data collected earlier in the day with the aide of a mobile weather station and data logger.

During the application period, there will be a total of 16 air samples collected; one sample taken from each of the 16 stationed air samplers. Air samplers will run for the duration of the methyl parathion application period and will also run an additional 3 hr post application time period to reduce staff exposure to the compound.

The post application period is the final sampling period and will consist of a total of 120 air samples collected over 8 sampling periods. At each sampling period, 16 air samples will be collected with sample run time set at 7am to 7pm over a four day period.

The use, operation, calibration and maintenance of air sampling pumps are described in SOP EQAI001.00. Preparation of sorbent tubes for use with air sampling pumps is described in SOP FSAI001.00. Air sampling tubes will contain XAD-4 resin. These filled tubes will be placed at a breathing height of 4-5 ft to collect residues of methyl parathion and methyl paraoxon. Aluminum foil sheets will encase the glass tubes to prevent photodegradation. All air sampling machines will be adjusted to a flow rate of 2

L/min or less for each sampling interval. Prior to each sampling period, flow rates will be checked with a rotometer and flow measurements recorded on the chain of custody as described in SOP ADMN006.00.

Total Number of Samples Collected per Study Site

(16 stations x 9 sampling intervals/station) + 1 station x 1 sample = 145 samples

Once samples are collected, the top and bottom tube openings for each air sample will be tightly capped and will be immediately placed on dry ice and remain frozen until extracted by the laboratory. All samples will be stored and transported in compliance with SOP QAQC004.01. Preparation and usage of temperature data loggers that are placed in ice chests to record temporary storage and transport temperatures are described in SOP EQOT001.01.

A mobile weather station will be transported and secured adjacent to the study field to collect meteorological data prior to the onset of the study and for the entire duration of the study. Wind speed, wind direction, ambient air temperature, and relative humidity will be collected using this instrument. Geographic measurements of the field location and air sampling locations will also be documented. The application equipment and conditions will be carefully described, as well as the inter-orchard route that the application follows.

Prior to pesticide application, soil samples will be collected to determine soil moisture, soil bulk density, soil texture, and soil organic matter content. Sample collection for bulk density and physical analysis is described in SOP FSSO002.00 and SOP FSSO001.00. Soil will be randomly collected to a one-inch depth in the field with the use of a steel core sampler with a known internal diameter. A maximum of 20 locations will be sampled in the field to collect the necessary data.

## **V. CHEMICAL ANALYSES**

The California Department of Food and Agriculture Center for Analytical Chemistry will perform the chemical analyses. The reporting limits for methyl parathion and methyl paraoxon in XAD-4 resin are 0.1 and 0.2 Fg/sample, respectively.

## **VI. DATA ANALYSES**

Air concentrations will be presented as micrograms of methyl parathion and methyl paraoxon per cubic meter ( $Fg/m^3$ ). Soil moisture, texture, and organic content will be presented as a percentage, and soil bulk density will be presented as grams per cubic centimeter (g/cc).

In addition, the weather data and measured methyl parathion and methyl paraoxon concentrations will be entered into the ISCST3 computer model. The ISCST3 model uses the flux rate, field size, weather, and terrain to simulate air concentrations. These studies will provide data on the field size, weather, terrain, and air concentrations, but not the flux rate. DPR will use the ISCST3 model to attempt to back-calculate an estimate of methyl parathion flux rates.

DPR will back-calculate flux rates by inputting the specific field dimensions, weather, and terrain data into the ISCST3 model, as well as an assumed flux value. The air concentrations simulated by the ISCST3 model (using the assumed flux value) will be regressed on the measured air concentrations. The slope of the regression line yields an adjustment or calibration factor for the assumed flux value used in the ISCST3 model. Using the calibrated flux value in the ISCST3 model gives the best match to the measured air concentrations. This flux calibration factor represents the flux rate for modeling purposes.

## **VII. ESTIMATED TIME TABLE**

Field Sampling	May through August 2002
Laboratory Analyses	May through September 2002
Data Analyses	September through December 2002
Report Preparation	December through February 2003

## **IX. REFERENCES**

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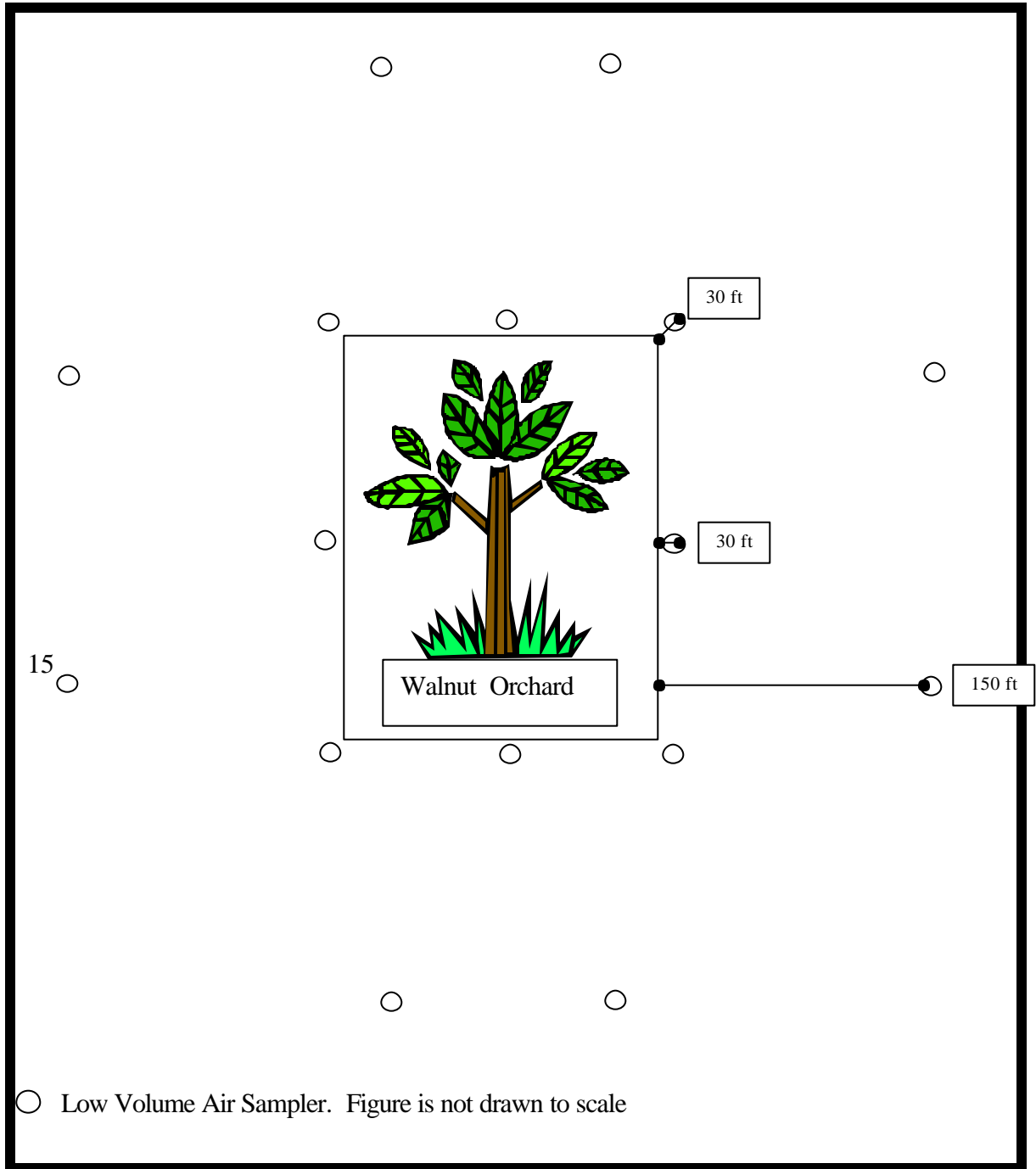


Figure 1. Location of 16 low volume air samplers around application area.