Department of Pesticide Regulation
Environmental Monitoring Branch
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STUDY #256: RESIDENTIAL INDOOR-OUTDOOR AND AMBIENT AIR MONITORING FOR PESTICIDE RESIDUES IN MENDOTA, CALIFORNIA

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I. INTRODUCTION

The Department of Pesticide Regulation (DPR) intends to conduct a collaborative monitoring study with the University of California, Davis (UCD) in Mendota, California. Incorporated in 1942, Mendota is situated approximately 35 miles due west of the city of Fresno in the northwestern portion of Fresno County, adjacent to the Madera County boundary line. Cotton, alfalfa, tomatoes, corn, and almonds are grown near this rural community.

Approximately 95% of the city's 9,788 residents are of Hispanic-Latino ethnicity, which is higher than the Hispanic-Latino ethnicity of 44 and 33% for Fresno County and California, respectively (Department of Finance, 2009). Mendota residents have an annual median family household income of $23,705 with approximately 35% of the city's families below the poverty line (United States Bureau of Census, 2000). The vast majority of Mendota inhabitants living in the 1.9 square mile area comprise the local agricultural labor force.

Residents living in this rural community are likely exposed to pesticide residues from agricultural production activities as well as residential pesticide applications taking place in this region. Consequently, DPR will collect air samples in Mendota for pesticide analysis. The Department has conducted previous air monitoring studies in Parlier and Lompoc, California and successfully used a multi-pesticide residue chemical analyses that reduced sampling and analytical costs for both studies (Table 1). Based upon the target compounds in the multi-residue analysis, there were approximately 300,000 pounds, 90,000 pounds, and 20,000 pounds of insecticides, herbicides, and fungicides, respectively, applied within 5-miles of Mendota in 2007 (Table 2).

Table 1. Target pesticides in multi-pesticide residue analysis

Pesticide Chemical Name	Example of Product Name	Pesticide Grouped by Type of Control	Pesticide Chemical Class
Chlorothalonil	Bravo	Fungicide	Chloronitrile
Chlorpyrifos	Dursban	Insecticide	Organophosphate
Chlorpyrifos Oxygen Analog	-		
Cypermethrin	Demon	Insecticide	Pyrethroid
Diazinon	Various Names	Insecticide	Organophosphate
Diazinon Oxygen Analog	-		
Dichlorvos	Vapona	Insecticide	Organophosphate
Dicofol	Kelthan	Insecticide	Organochlorine
Dimethoate	Cygon	Insecticide	Organophosphate
Dimethoate Oxygen Analog			
Diuron	Karmex	Herbicide	Urea
Endosulfan	Thiodan	Insecticide	Organochlorine
Endosulfan Sulfate	-		
EPTC	Eptam	Herbicide	Carbamate
Malathion	Various Names	Insecticide	Organophosphate
Malathion Oxygen Analog	-		
Metolachlor	Dual	Herbicide	Chloracetanilide
Molinate	Ordram	Herbicide	Thiocarbamate
Naled (dichlorvos)	Dibrom	Insecticide	Organophosphate
Norflurazon	Solicam	Herbicide	Pyridazinone
Oryzalin	Surflan	Herbicide	Dinitroaniline
Oxyfluorfen	Goal	Herbicide	Diphenyl ether
Permethrin	Ambush	Insecticide	Pyrethroid
Phosmet	Imidan	Insecticide	Organophosphate
Propanil	Duet	Herbicide	Anilide
Propargite	Omite	Insecticide	Organosulfite
Simazine	Princep	Herbicide	Triazine
SSS-tributylphosphorotrithioate	DEF	Defoliant	Organophosphate
Thiobencarb	Bolero	Herbicide	Thiocarbamate

Table 2. Target pesticides used within 5-mile distance of Mendota city boundary

Pesticides Grouped by Type of Control	Pesticide Chemical Name	Pounds of Product Applied per Year			Sum
		2005	2006	2007	
INSECTICIDE	Chlorpyrifos	36,489	33,910	22,733	93,133
	Cypermethrin	0	12	0	12
	Diazinon	5,338	5,949	547	11,834
	Dicofol	15,161	11,294	6,306	32,761
	Dimethoate	2,331	1,760	1,421	5,512
	Endosulfan	4,510	3,784	2,028	10,322
	Imidacloprid	782	1,271	4,063	6,116
	Malathion	23,495	243,701	253,483	520,678
	Naled	11,435	5,765	677	17,877
	Permethrin	55	594	97	746
	Phosmet	0	640	0	640
	Sum	99,596	308,680	291,355	
HERBICIDE	Diuron	9,360	9,724	11,096	30,180
	EPTC	0	0	3,256	3,256
	Oryzalin	2,231	2,900	7,211	12,342
	Oxyfluorfen	12,813	12,653	11,108	36,573
	Simazine	25	25	6	57
	Trifluralin	85,470	97,923	57,182	240,574
	Sum	109,899	123,205	89,859	
FUNGICIDE	Chlorothalonil	2,107	7,874	20,287	30,267
DEFOLIANT	s,s,s-Tributyl Phosphorotrithioate	1,483	3,490	963	5,936

The UCD's Department of Public Health Sciences Center for Health and Environment staff has been assessing 400 Mendota farm workers and their families for the past 5 years. The MICASA (translated from Spanish to English is equivalent to "my home") study team collects occupational and environmental data in an effort to improve farm workers' overall work place health and farm safety, as many of the residents are immigrants from Mexico or Central America.

In Spring 2009, MICASA staff will evaluate farm laborer dust exposure at several different farms in order to quantify particulate levels associated with various agricultural activities. In addition, indoor dust samples will be collected from 125 participants' homes, along with food and urine samples from the household's mother and one of her children in an attempt to identify various routes of permethrin exposure. This pesticide has agricultural and home use applications.

II. OBJECTIVE

The DPR's objectives for this collaborative study are to; 1) collect indoor and outdoor residential air samples for pesticide residues and to compare their concentrations, 2) collect ambient air for pesticide residues and compare results to indoor-outdoor residential air monitoring results, and 3) obtain pesticidal home use information (UCD objective) and nearby agricultural use records so that these data can be related to indoor-outdoor, and ambient pesticide air concentrations.

III. PROJECT PERSONNEL

This project will be conducted by personnel from DPR's Environmental Monitoring Branch under the general direction of the Project Supervisor, Pam Wofford, Senior Environmental Scientist. Other key personnel assigned to the project include:

Project Leader:	Clarice Ando
Field Coordinators:	Shifang Fan
	Roger Sava
Research Scientist:	Bruce Johnson
Statistician:	Jing Tao
Laboratory Liaison:	Sue Peoples
Chemical Analysis:	Department of Food and Agriculture, Center for Analytical Chemistry

All questions concerning this protocol should be directed to Pam Wofford at (916) 324-4297 or e-mail address; pwofford@cdpr.ca.gov.

IV. STUDY PLAN

UCD staff anticipates collecting indoor residential dust, food, and urine samples from Mendota participants beginning June 2009. Study information will be gathered from 125 homes with UCD staff making preliminary visits to 2-4 homes on Monday and Tuesday of each week. UCD data collection begins the day following preliminary contact, with the UCD study concluding at each residence on Wednesday and Thursday, respectively (24-hr period).

DPR staff will follow UCD staff to 2 homes on Monday and Tuesday to set-up air sampler pumps at each residence which have fenced backyards. One air sampler pump will be placed inside the home and another pump will be placed outside of each monitored residence, in the backyard. To reduce disturbing study participants, all residential indoor-outdoor air sampler pumps will be connected to an automatic timer so

that air samplers will begin operation at a designated time on Tuesday and Wednesday for sites set-up on Monday and Tuesday, respectively. At the conclusion of the 24-hr sampling period at each residence, DPR staff will enter the home site (Wednesday and Thursday) with UCD staff. DPR will collect indoor-outdoor air samples at that time. Study sites will include residential homes and other types of housing with enclosed backyards.

Two air samplers will be placed within the Mendota community to monitor ambient pesticide residue levels. Based upon the geographic location of the study homes within the Mendota community, there is preference to have a centrally located sampler and another placed on the northeastern region of the monitored residences. Ambient samplers will be positioned 7-50 ft above the ground and will be at least 70 ft from obstacles such as trees so that air flow is unobstructed. All indoor, outdoor, and ambient monitoring locations will be accessible to DPR staff during the study, have accessible electrical outlets, offer security from vandalism, and have permission of the resident/owner.

Air Monitoring Equipment and Equipment Set-Up

Aircheck air sampler pumps will be used to draw in air at a rate of 10 Liters/minute to capture residues for the multi-residue pesticide analysis. Air will pass through a glass sampling tube containing 30 ml of XAD-4 adsorbent resin material held in place by a wire mesh-screen bottom and glass wool plug on top. Sample labels printed with the study and sample identification number will be secured to the outside of each sample tube. Tubes used for outdoor sampling will be wrapped with an aluminum foil sheet to reduce degradation of pesticides due to light exposure. Preparation of air sampling tubes is described in DPR's SOP field sampling (FSA) I001.01 (Ganapathy, 2003).

Indoor air sampler pumps will be enclosed inside a 30-gallon plastic trash receptacle with a snap-on lid. A small opening through the lid surface will allow the air sampling stand and accompanying sample tube to stand upright and extend 3-4 feet (ft) above the residence floor and reduce operating noise. Two 5-pound sand bags will also be placed in the bottom of each receptacle to lessen the chance of being over-turned by children in the home.

Samplers will be located in the center of the family room or any other room that is an area of daily congregation by study participants. There shall be no windows, doors, fans, or other objects within 5 ft of the air sampler.

Outdoor air samplers will only be placed at single story residences with fenced backyards offering security to sampling equipment. Preferably, the sampler will be placed in the center of the backyard away from windows, doors, air conditioner units, vents, or fans. The air sampling tube will be 3-4 ft above ground level.

When air sampling commences at each location, the sample number, sample date, time, equipment number, staff initials, weather conditions, location of air sampler inside/outside residence, and flow rate will be documented on the chain of custody (COC) form. At the end of the sampling period, the ending flowrate will also be documented on the COC along with the sample date, time, and staff initials. A DryCal

primary flowmeter will be used to measure the sample flow rates at the starting and ending sample periods. A valid air sample pump will operate with less than a 20% difference from the recorded starting and ending flow rates.

Collected sample tubes will have both tube ends corked with rubber stoppers while in the field and samples will then be placed into a storage unit containing dry ice. At the end of weekly sampling, air samples will be transported to the DPR's Sacramento facility, where samples will be checked in and placed into a freezer unit. Sample handling and shipping will follow procedures defined in DPR's SOP quality assurance quality control (QAQC) 003.02 (Ganapathy, 2005).

Additional Environmental Sampling

Meteorological measurements will be taken using a MetOne meteorological station located at the edge of Mendota. Sensors will be placed atop a 33 ft mast to measure wind direction, horizontal wind speed, temperature, solar radiation, and relative humity at 1 minute intervals. Information will be recorded on a Campbell Scientifoc CR21 Datalogger as 5 minute averages.

Indoor and outdoor humidity levels at each residence will be monitored at the time of air sampler set-up and take-down using a thermohygrometer. Temperature will be tracked inside each residence during the sampling interval using a HOBO secured to the side of the trash receptacle.

Additional information at each residence will be recorded. Information would include living room dimensions, presence of air conditioner, air conditioner operating at time of visit, location of air sampler in living room, backyard dimensions, placement of air sampler in backyard and other observed or measured data (Figure 1).

Field Sampling Quality Control

Three types of ongoing quality control samples will be routinely collected in the field during the monitoring study; trip blank samples, fortified field spikes, and co-located duplicate samples. A trip blank is a sample tube containing no pesticide residue. Upon collection of all field samples for that sampling period, the trip blank will be co-mingled on dry ice with the collected air samples inside the storage container. All samples remain together until receipt at DPR's Sacramento facility. If pesticide residue is detected in the trip blank sample, action will take place to reassess field and laboratory procedures.

A fortified field spike is a sample tube prepared by the laboratory containing a known quantity of pesticide(s) on the XAD-4 resin. It will be delivered to the field on dry ice and placed on an air sampler with air flowing through the sample tube during the air sampling period at a single location. At the end of the sampling period, all field samples and the fortified spike are collected, stored, and shipped together. The pesticide recovery for the fortified spike in relation to the recovery of the field sample at the same identical location, provides some information about any change in the ability to recover the analyte when exposed to field conditions. Reassessment of the field and laboratory procedures will occur when fortified field spike sample pesticide recoveries fall outside the control limits established from the validation data for each pesticide.

Name_____
Address_____

I. INDOOR

A. Distance to:
- a. Nearest wall_____
- b. Nearest window_____
- c. Nearest outside door_____
- d. Fireplace_____

B. Air sampler tube's height above floor_____
C. AC unit present?_____
D. AC unit in operation at time of visit?_____
E. Windows open at time of visit?_____
F. Smokers in home based on odor?_____

II.OUTDOOR

A. Distance to nearest window_____
B. Distance to fence_____
C. Type of windows_____
D. AC unit present?_____
E. Type of residence (slab, crawl space, mobile home, single family residence, single story)

Please sketch a diagram of the residence and placement of air sampler inside and outside home. Include measurements to walls and other obstacles.

Figure 1. Information –diagram sheet to be completed at each residence

A duplicate sample is a blank sample that is co-located with a field sample at the same location using an identical air sampler pump as that used with the field sample. Pesticide recovery from the duplicate and field samples are used to evaluate laboratory analytical precision. Samples having a greater than 50% difference in pesticide residue concentration from the duplicate and field sample will result in the reassessment of the field and laboratory procedures.

Quality control samples will be collected on a routine schedule with one trip blank, or one fortified field spike, or one co-located duplicate sample collected each week

Pesticide Use Data

DPR will obtain pesticide use information for agricultural pesticides applied during the monitoring period within a 1, 5, and 10-mile radius around the city of Mendota. Information will originate from county agricultural commissioners' staff located in Fresno and Madera. Use information will be gathered on a townhip, range, and section basis.

V. CHEMICAL ANALYSES

Laboratory Analytical Methods

The California Department of Food and Agriculture Center for Analytical Chemistry (CDFA laboratory) will perform chemical analysis for the air samples. Extraction and analytical methods for the XAD-4 resin are located in standard operating procedure SOP Environmental Monitoring (EMON) SM 05-002. Pesticide analysis will involve a liquid chromatograph-mass spectrometer, and gas chromatograph-mass selective detector following ethyl acetate extraction of the XAD-4 resin. Greater detailed analytical methods will be presented in the final report.

Quality Assurance

CDFA laboratory staff will follow DPR's standard laboratory quality control procedures as outlined in SOP QAQC001.00. The analytical method's precision and accuracy were validated using sample air tubes spiked at 3 different concentrations for each pesticide and breakdown product. Trapping efficiency tests were also preformed to determine if pesticide residue remained trapped on the XAD-4 resin and breakthrough did not occur. Storage stability tests were conducted on pesticide spiked air samples stored at -4ºC for varying lengths of time to determine if and when degradation occurred, indicating that field samples should be taken out of storage and analyzed prior to breakdown.

During analyses of field samples ($\leq$ 10 samples per batch), quality control samples will also be submitted for analyses. This includes pesticide spiked samples to provide checks on analytical precision and accuracy and blank samples to provide information on possible contamination.

Method Detection Limit and Limit of Quantitation

The method detection limit for each pesticide was determined by CDFA laboratory staff by analyzing a pesticide standard at a concentration with a signal to noise ration of 2.5 to 5. A spiked air sample was analyzed at least seven times and the method detection limit was determined by calculating the 99% confidence interval of the mean as is described in United States Environmental Protection Agency (US EPA, 1990). The limit of

quantitation was set at a certain factor above the method detection limit, with the level of interference found in the samples determining this factor. The method detection limit and limits of quantitation for each pesticide are given in Table 3.

Table 3. List of pesticide compounds in the multi-residue analysis and their associated detection and quantitation limits for CDFA Laboratory

Pesticide Chemical Name	CDFA Laboratory Detection Limit (ng/m^3)	CDFA Laboratory Quantitation Limit (ng/m^3)
Chlorothalonil	13.7	46.3
Chlorpyrifos	5.05	46.3
Chlorpyrifos oxygen analog	2.92	11.6
Cypermethrin	4.68	46.3
Diazinon	1.16	4.63
Diazinon oxygen analog	2.08	4.63
Dichlorvos (Naled)	3.24	46.3
Dicofol	2.13	46.3
Dimethoate	2.31	4.63
Dimethoate oxygen analog	1.94	4.63
Diuron	5.14	23.2
Endosulfan	3.24	46.3
Endosulfan sulfate	4.63	46.3
EPTC	1.67	4.63
Malathion	2.18	11.6
Malathion oxygen analog	1.30	4.63
Metolachlor	2.73	11.6
MITC	5.56	23.2
Molinate	1.81	4.63
Norflurazon	3.75	11.6
Oryzalin	1.39	4.63
Oxyfluorfen	6.39	46.3
Permethrin	7.22	46.3
Phosmet	7.96	23.2
Propanil	2.31	11.6
Propargite	3.8	46.3
Simazine	1.20	4.63
sss-tributylphosphortrithioate	1.76	4.63
Thiobencarb	5.60	11.6
Trifluralin	1.67	23.2

DATA PRESENTATION AND ANALYSIS

Air concentrations for each pesticide will be presented in ng/m^3. Non parametric statistics will be used compared to indoor, outdoor, and ambient air residue levels for each pesticide detected.

Means and standard deviations will be computed from collected data. Data will be compared using charts. It is anticipated that data will be non-normal and contain numerous non-detects. For these reasons, statistical comparisons will be based on non-parametric tests such as the Wilcoxon signed rank test (Sokal and Rohlf, 1981).

III. TIMETABLE

Field Sampling:	June 2009 – September 2009
Chemical Analysis:	June 2009 – October 2009
Final Report:	August 2010

IX. REFERENCES

California Department of Finance. 2009. 2008 California Statistical Abstract. 48th Edition. Sacramento, California.

Ganapathy, C. 2003. Preparation of air sampling tubes and resin jars. SOP – field sampling air. 1001.01. CDPR. Sacramento, CA

Ganapathy, C. 2005. Sample tracking procedures. SOP QAQC 003.02. CDPR. Sacramento, CA

Sokal, R.R. and F. J. Rohlf. 1981. Biometry. W.H. Freeman and Company. New York, New York.

United States Bureau of the Census. 2000. http://www.census.gov/