

**AIR RESOURCES BOARD**2020 L STREET  
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## MEMORANDUM

TO: Dr. John Sanders, Chief  
Environmental Monitoring and Pest Management Branch  
Department of Pesticide Regulations

FROM: George Lew, Chief *George Lew*  
Engineering and Laboratory Branch

DATE: November 9, 1995

SUBJECT: CARBOFURAN AMBIENT MONITORING FINAL REPORT

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Attached is the final report, "Ambient Air Monitoring for Carbofuran in Imperial County During February and March 1995."

If you or your staff have questions or need further information, please contact me at 263-1630 or Don Fitzell at 263-2041.

## Attachment

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AIR RESOURCES BOARD

**Ambient Air Monitoring for Carbofuran in Imperial County  
During February and March 1995**

Engineering and Laboratory Branch  
Monitoring and Laboratory Division

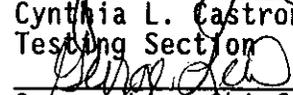
Test Report No. C93-013

Report Date: November 9, 1995

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This report has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Ambient Air Monitoring for Carbofuran in Imperial County  
During February and March 1995

This report presents the results of ambient air monitoring in Imperial County for carbofuran during the peak use period of February and March. Samplers were set up in various towns near expected application sites. Of the more than 80 samples collected, nineteen were found to be above the minimum detection limit, 0.25 ug/sample (approximately 0.012 ug/m<sup>3</sup> for a 24-hour sample). Nine of the nineteen values above the detection limit as well as the maximum value detected, 0.11 ug/m<sup>3</sup>, were found at the APCD PM-10 site. Eight of the remaining ten values above the detection limit were found at the Meadows Union School. The El Centro and Calipatria sites each had one sample above the detection limit. No detectable carbofuran was found at Heber.

## Acknowledgments

Jack Rogers and Jack LaBrue were the Instrument Technicians. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Air Quality Measures Branch as well as the Imperial County Agricultural Commissioner's Office. Chemical analyses were performed by the Trace Analytical Laboratory of the Department of Environmental Toxicology at U.C. Davis.

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Ambient Air Monitoring for Carbofuran in Imperial County  
During February and March 1995

I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Air Quality Measures Branch, the ARB Engineering and Laboratory Branch (ELB) conducted a four-week ambient monitoring program for carbofuran in Imperial County during the Winter of 1995. This monitoring occurred from February 14 through March 10, 1995. The peak use of carbofuran is during the winter as an insecticide on alfalfa. As required by the Food and Agricultural Code 14021, this monitoring was conducted to provide the DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

Additional data was provided last year for an application monitoring of this pesticide. The report is, "Ambient Air Monitoring for Carbofuran in Imperial County during Spring 1993, after an Application to an Alfalfa Field."

II. DESCRIPTION

Carbofuran (molecular weight 221.26 g/mole) is a broad spectrum insecticide used on various crops for a variety of pests. It is a white, odorless solid with a melting point of 153-154°C, and a vapor pressure of  $3.1 \times 10^{-7}$  mbar at 20°C. Carbofuran is nearly insoluble in water and n-hexane, but is soluble in 2-propanol and readily soluble in dichloromethane. The oral LD<sub>50</sub> for rats is approximately 8 mg/kg and the dermal LD<sub>50</sub> is >3,000 mg/kg (1994 Farm Chemicals Handbook).

Carbofuran is regulated as a restricted use material under section 6400, Title 3 of the California Code of Regulations, requiring a permit to purchase products containing greater than 10% active ingredient (carbofuran) by weight.

III. SAMPLING LOCATIONS

The 1993 Pesticide Use Report (PUR) indicated that the highest usage of carbofuran occurred in Imperial County during the winter months. This information along with the recommendations of the Imperial County Agricultural Commissioner's Office was used to determine which locations would be expected to be near carbofuran applications. As a result five sites were selected: one in Calipatria (site C), one half way between El Centro and Holtville at the Meadows Union School (site M), one in Heber (site E), one northeast of El Centro at an APCD PM-10 site (site PM) and one in El Centro (site EC) which was the urban background site. All samplers were on roof tops (approximately 15 feet above ground) except the PM-10 site which was on ground level (approximately 1.5 meters above ground). TABLE I lists the addresses or locations of the monitoring sites. FIGURE I shows the location of

these monitoring sites. In addition, a second sampler was located at Calipatria to obtain duplicate collocated samples which were used to evaluate the precision of the data.

The sites were chosen on the basis of the criteria listed in the QA Plan for Pesticide Monitoring (APPENDIX I, Attachment II). Other considerations in selecting the monitoring sites were: proximity to expected application sites, possible population exposure, reasonable access, availability of AC power, and security.

#### IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through a Teflon holder containing approximately 30 cc of XAD-4 resin (see APPENDIX I). The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any carbofuran present in the sampled ambient air was captured by the XAD-4 adsorbent. Subsequent to sampling, the resin was transferred into a glass jar with a Teflon-lined lid and stored in an ice chest containing dry ice. At the end of each week, all samples were shipped on dry ice to the Trace Analytical Laboratory (TAL) of the Department of Environmental Toxicology, U.C. Davis for analysis.

Each sample train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, rotometer, train support, and a 115VAC powered vacuum pump. A diagram of the sampling train is shown in APPENDIX I, Attachment I. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow was adjusted with a metering valve to an indicated reading of 15.0 on the rotometer. A leak check was performed by blocking off the flow meter inlet. Upon completion of a successful leak check, the indicated flow rate was again set at 15.0 and was recorded (if different from the planned setting) along with date, time and site location. Calibration prior to use in the field indicated that an average flow rate of 14.7 lpm was actually achieved when the flow meter was set to 15.0. Each sampler was run at this rate for approximately 24 hours. At the end of each sampling period the final indicated flow rate (if different than the set 15.0), stop date, and time were recorded. Samples were run Monday through Friday, collecting four samples per week.

#### V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the TAL staff. The XAD-4 resin was extracted with 75 ml of ethyl acetate. A clean up procedure was required for field samples through use of a Florisil column. Analysis was completed using gas chromatography. Separation was accomplished using either a DB-5 Megabore column or a XTI-5 column. Measurement was with a nitrogen/phosphorus detector and confirmation of some samples with gas chromatography/mass selective

detector. A detailed description of the analytical procedure is presented in APPENDIX II.

All samples were shipped on dry ice, at the end of each week, to the analytical laboratory where they were immediately extracted then analyzed. Stability studies conducted by the laboratory indicated no loss of sample for up to twelve days. However, one set of samples (series 11-14) was inadvertently shipped to Memphis by FED EX and not received by the laboratory until 48 hours later than anticipated (see APPENDIX II).

## VI. RESULTS

Results for carbofuran are shown in TABLE II and APPENDIX II. A summary of the results is shown in TABLE III. The QA/QC data are presented in TABLE IV.

The reported values (TABLE II) were calculated using the average of the beginning and ending flow rates. All corrected flow rates (where measurable carbofuran was reported) were within 10% of the original flow rate.

Of the 84 samples taken, nineteen were found to be above the minimum detection limit, 0.25 ug/sample (approximately 0.012 ug/m<sup>3</sup> for a 24-hour sample). Nine of the nineteen values above the detection limit as well as the maximum value detected, 0.11 ug/m<sup>3</sup>, were found at the APCD PM-10 site. Eight of the remaining ten values above the detection limit were found at the Meadows Union School. The El Centro and Calipatria sites each had one sample above the detection limit. No detectable carbofuran was found at Heber.

## VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Laboratory Report for carbofuran (APPENDIX II).

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX I, Attachment II) were followed. Field spikes were prepared by the TAL staff, transported to the sampling sites by ARB staff and shipped the same as field samples to Sacramento. Laboratory spikes were prepared by the Quality Management and Operations Support Branch (QMOSB) of the ARB. The field spikes ranged from 99% to 122% recovery while the QMOSB audit spikes ranged from 79% to 100% recovery. The complete results for both sets are shown in TABLE IV.

TABLE I. Carbofuran Ambient Monitoring Sites

Site ID	Address
C	Calipatria Fire Station 125 N. Park Calipatria, CA 92233
M	Meadows Union School S-80 at Bowker Road Holtville, CA 92250
EC	APCD/Agricultural Commissioner's Office 150 S. 9th St. El Centro, CA 92243
H	Felipe & Ramon Primary School 10th St. and Heber Ave. Heber, CA 92249
PM	APCD PM-10 Ambient Monitoring Station approximately 0.1 miles north of the intersection of Harris and McConnell Roads

TABLE II. Carbofuran Ambient Monitoring Data

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
1C1	1425	20.9	0.64	0.031	2/14-15/95
1C2	1425	20.9	ND	---	
1M	1425	20.9	0.48	0.023	
1EC	1430	21.0	ND	---	
1H	1445	21.2	ND	---	
1PM	4335	63.7	0.28	0.0044	
2C1	1405	20.7	ND	---	2/15-16/95
2C2	1405	20.7	ND	---	
2M	1500	22.0	ND	---	
2EC	1420	20.9	ND	---	
2H	1420	20.9	ND	---	
2PM	Sample unable to be collected. See sample 1PM.				
2B	BLANK	--	ND	X	
3C1	1425	19.3*	ND	---	2/16-17/95
3C2	1425	20.9	ND	---	
3M	1445	21.2	ND	---	
3EC	1450	21.3	ND	---	
3H	1395	20.5	ND	---	
3PM	Sample unable to be collected. See sample 1PM.				
4C1	1325	17.5*	ND	---	2/21-22/95
4C2	1325	19.5	ND	---	
4M	1330	18.0*	0.48	0.027	
4EC	1330	19.6	ND	---	
4H	1330	18.0*	ND	---	
4PM	1335	19.6	1.64	0.084	
5C1	1335	19.6	ND	---	2/22-23/95
5C2	1335	19.6	ND	---	
5M	1335	19.6	0.27	0.014	
5EC	1325	18.0*	ND	---	
5H	1330	19.6	ND	---	
5PM	1330	19.6	1.59	0.081	
6C1	1350	19.8	ND	---	2/23-24/95
6C2	1350	19.8	ND	---	
6M	1330	19.6	0.34	0.017	
6EC	1325	19.5	0.28	0.014	
6H	1320	19.4	ND	---	
6PM	1335	19.6	2.14	0.11	
6B	BLANK	--	ND	X	

<sup>1</sup>C = Calipatria, M = Meadows Union School, EC = El Centro, H = Heber, PM = APCD PM-10 ambient air monitoring site. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 14.7 liters per minute unless noted otherwise.

<sup>3</sup>ND = Not Detected, <0.25 ug/sample (approx. 0.012 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

\*Final flow rate different from set value of 14.7 lpm. Volumes corrected.

TABLE II. Carbofuran Ambient Monitoring Data (Cont.)

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
7C1	1230	18.1	ND	---	
7C2	1230	18.1	ND	---	
7M	1330	18.1	0.30	0.017	
7EC	1435	21.1	ND	---	2/27-28/95
7H	1390	20.4	ND	---	
7PM	1270	18.7	0.52	0.028	
7B	BLANK	--	ND	---	
8C1	1380	20.3	ND	---	
8C2	1380	20.3	ND	---	
8M	1385	20.4	0.34	0.017	
8EC	1385	20.4	ND	---	2/28-3/1/95
8H	1390	20.4	ND	---	
8PM	1370	21.1*	0.37	0.018	
9C1	1375	20.2	ND	---	
9C2	1375	20.2	ND	---	
9M	1365	20.1	ND	---	
9EC	1385	20.4	ND	---	
9H	1380	20.3	ND	---	3/1-2/95
9PM	1385	20.4	ND	---	
10C1	1370	20.1	ND	---	
10C2	1370	20.1	ND	---	
10M	1375	20.2	ND	---	
10EC	1350	19.8	ND	---	
10H	1355	18.4*	ND	---	3/2-3/95
10PM	1375	20.2	0.35	0.017	
11C1	1380	18.7*	ND	---	
11C2	1380	20.3	ND	---	
11M	1380	18.7*	ND	---	
11EC	1375	18.6*	ND	---	
11H	1375	20.2	ND	---	3/6-7/95
11PM	1380	18.7*	ND	---	
11B	BLANK	--	ND	---	
12C1	1380	18.7*	ND	---	
12C2	1380	20.3	ND	---	
12M	1370	18.6*	ND	---	
12EC	1360	18.4*	ND	---	
12H	1365	18.0*	ND	---	3/7-8/95
12PM	1370	18.1*	ND	---	

<sup>1</sup>C = Calipatria, M = Meadows Union School, EC = El Centro, H = Heber, PM = APCD PM-10 ambient air monitoring site. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 14.7 liters per minute unless noted otherwise.

<sup>3</sup>ND = Not Detected, <0.25 ug/sample (approx. 0.012 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

\*Final flow rate different from set value of 14.7 lpm. Volumes corrected.

TABLE II. Carbofuran Ambient Monitoring Data (Cont.)

Sample <sup>1</sup>	Time	Volume <sup>2</sup>	Total <sup>3</sup>	Concentration	Collection Dates
ID	(min.)	(m <sup>3</sup> )	(ug)	(ug/m <sup>3</sup> )	
13C1	1360	18.4*	ND	--	
13C2	1360	20.0	ND	--	
13M	1355	19.9	0.54	0.027	
13EC	1360	20.0	ND	--	3/8-9/95
13H	1360	16.6*	ND	--	
13PM	1355	17.9*	0.30	0.017	
14C1	1380	18.2*	ND	--	
14C2	1380	20.3	ND	--	
14M	1390	20.4	0.36	0.018	
14EC	1385	20.4	ND	--	3/9-10/95
14H	1390	20.4	ND	--	
14PM	1385	18.3*	0.34	0.019	

<sup>1</sup>C = Calipatria, M = Meadows Union School, EC = El Centro, H = Heber, PM = APCD PM-10 ambient air monitoring site. -1, -2 indicates duplicates taken at the same site.

<sup>2</sup>All flows at 14.7 liters per minute unless noted otherwise.

<sup>3</sup>ND = Not Detected, <0.25 ug/sample (approx. 0.012 ug/m<sup>3</sup>).

No values corrected for percentage of recovery.

\*Final flow rate different from set value of 14.7 lpm. Volumes corrected.

TABLE III. Summary of Carbofuran Ambient Data

Location	Number of 24-hour sampling periods	Number of samples above MDL <sup>a)</sup>	Maximum (ug/m <sup>3</sup> )	Average <sup>b)</sup> (ug/m <sup>3</sup> )
Calipatria	14	1	0.015	0.015
Meadows Union School	14	8 ✓	0.027	0.020
El Centro (urban background)	14	1	0.014	0.014
Heber	14	0	--	--
APCD PM-10 site	12	9	0.11	0.042

Collocated samples are averaged and used as a single sample for all data in this table. Non-detected calculated as zero.

a) MDL (Minimum detection limit) = 0.25 ug/sample (approx. 0.012 ug/m<sup>3</sup>).

b) Only samples above MDL included.

TABLE IV. QA/QC Data

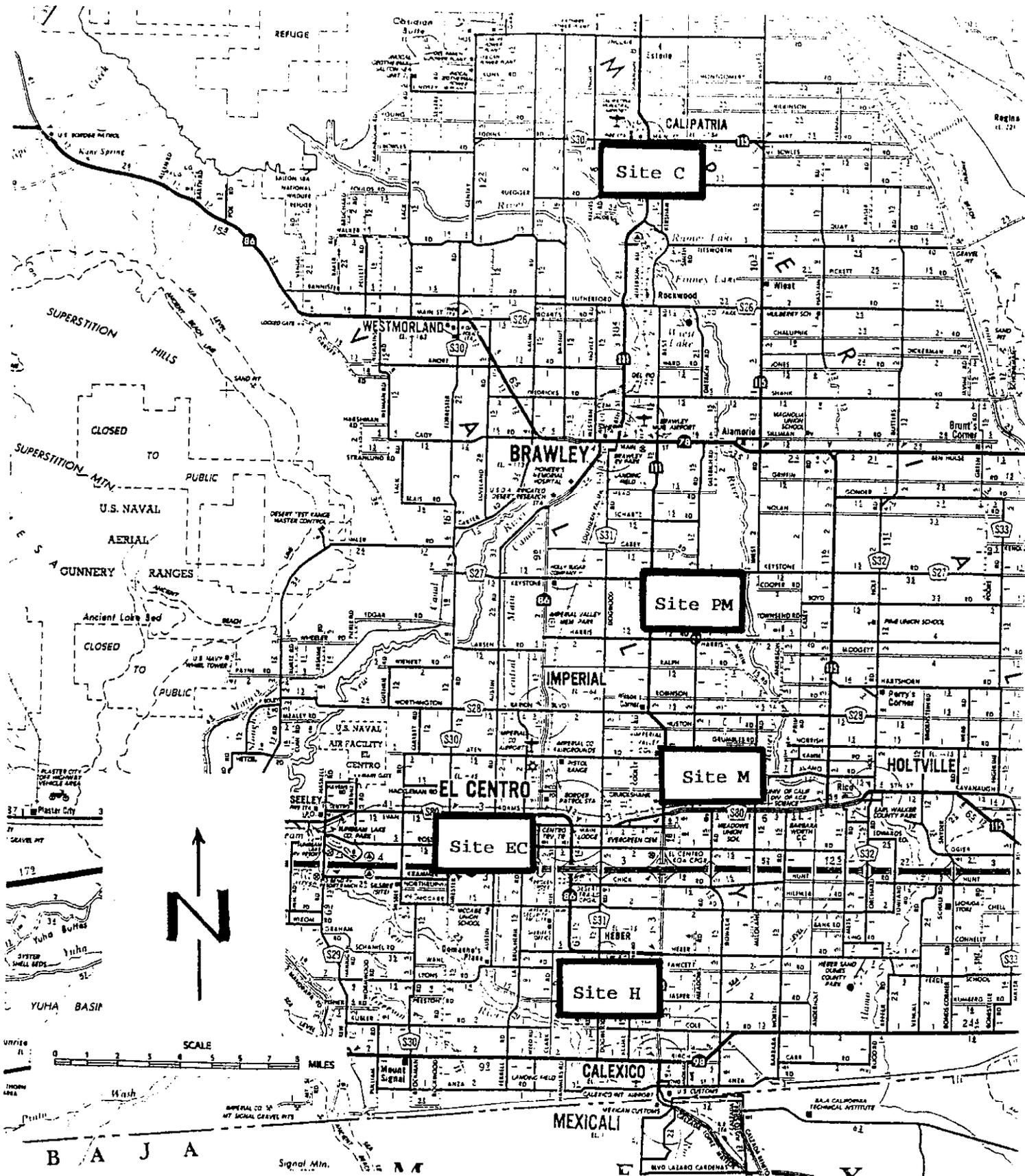
Field Spikes

Spike Level	Recovered	%
1.0 ug	1.12 ug	112
1.0 ug	1.07 ug	107
1.0 ug	1.04 ug	104
1.0 ug	1.22 ug	122
10.0 ug	10.4 ug	104
10.0 ug	10.3 ug	103
10.0 ug	9.9 ug	99
10.0 ug	10.1 ug	101

QMOSB Audit Spikes

Sample ID	Spike Level	Recovered	%
Carbo 1	6.25 ug	5.39 ug	86
Carbo 2	3.75 ug	2.96 ug	79
Carbo 3	8.75 ug	7.75 UG	89
Carbo 4	3.75 ug	3.16 ug	84
Carbo 5	6.25 ug	5.67 ug	91
Carbo 6	0.00 ug	<0.25 ug	--
Carbo 7	8.75 ug	8.72 ug	100

FIGURE I. Carbofuran Monitoring Area



APPENDIX I  
SAMPLING PROTOCOL

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

Pesticide Monitoring Protocol  
Carbofuran Ambient Air Monitoring in Imperial County  
During the Winter of 1995

Engineering and Laboratory Branch  
Monitoring and Laboratory Division

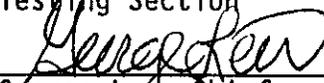
Project No. C93-013

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Carbofuran Ambient Air Monitoring in Imperial County  
During the Winter of 1995

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch (TACIB), the ARB Engineering and Laboratory Branch (ELB) staff will conduct ambient air monitoring for carbofuran in Imperial County. The monitoring program is being conducted to support DPR's toxic air contaminant program. Section 14022(c) of the Food and Agriculture Code requires the ARB "to document the level of airborne emissions .... of pesticides which may be determined to pose a present or potential hazard..." when requested by the Department of Pesticide Regulation. The test program is tentatively scheduled for four weeks in February-March 1995.

The ambient monitoring for carbofuran is the second part of the two-phase pesticide and monitoring program. The first monitoring was conducted in the spring of 1993 near a specific application of carbofuran to assess maximum acute concentrations. A report summarizing those results is available from the ARB ("Ambient Air Monitoring for Carbofuran in Imperial County during Spring 1993, after an Application to an Alfalfa Field.") This second phase, ambient monitoring, is to determine the general population exposure to carbofuran, if any.

Carbofuran is a broad spectrum insecticide used on various crops for a variety of pests. The 1992 Pesticide Use Report indicated it was predominately used on alfalfa, followed by grapes, rice, and artichokes. The peak use of carbofuran on alfalfa occurs during February and March in Imperial County. Carbofuran is regulated as a restricted use material under Section 6400, Title 3 of the California Code of Regulations, requiring a permit to purchase products containing greater than 10% active ingredient (carbofuran) by weight.

II. Sampling

Three to five samplers will be set up at various locations throughout Imperial County. Sampling sites will be selected based upon criteria outlined on page 4 of the "Quality Assurance Plan for Pesticide Monitoring" (Attachment II). Monitoring sites will be located in areas near expected pesticide application sites where the public exposure may occur. Twenty-four hour samples will be taken Monday through Friday at a flow rate of approximately 15 liters/minute.

ARB staff will conduct the sampling based on the methodology developed by the University of California, Davis. The sampling equipment will consist of a rotometer, Teflon sample holder and a 115VAC vacuum pump (see Attachment I). The pump will draw air through the sampling equipment. Calibrated rotometers will be used to measure sample flow rates. Thirty milliliters of cleaned XAD-4 resin, contained in a Teflon holder will be used to capture the pesticide. Sampling equipment will be leak checked prior to and after each sampling period with the sampling media installed.

Any change in the flow rates will be recorded in the field log book. ELB staff will record in the field log book the start and stop times, sample identifications and any other significant data.

After collecting 24-hour samples, ELB staff will remove the XAD-4 resin from the Teflon holder, transfer the resin into a glass jar with a Teflon-lined lid, and store the resin in an ice chest containing dry ice. At the end of each week, the samples will be shipped by overnight mail service to the University of California, Davis for analysis. The samples will be sent in an insulated container containing dry ice. Upon receipt of the samples, The University of California, Davis laboratory staff will store the samples in a freezer until analysis.

III. Analysis

Under contract to the ARB, the staff at the Trace Analysis Laboratory, Department of Environmental Toxicology, University of California, Davis will analyze the samples for carbofuran. Dr. Takayuki Shibamoto, the principle investigator, will direct Mr. Chuck Mourer and other staff in the analysis. All samples will be stored in an ice chest containing dry ice or in a freezer until analysis. The XAD-4 resin collected will be extracted with 75 ml of ethyl acetate, the extract concentrated, followed by gas chromatography separation on a DB-5 column. Carbofuran will be determined by a Thermionic Specific (nitrogen/phosphorous) Detector (TSD or NPD). The Standard Operating Procedure (S.O.P.) for the analysis of carbofuran is contained in the previous report, "Ambient Air Monitoring for Carbofuran in Imperial County During Spring 1993, After an Application to an Alfalfa Field" and will be included in the final report of this monitoring.

IV. Quality Assurance

Field sampling and analytical laboratory procedures will follow ARB's "Quality Assurance Plan for Pesticide Monitoring." The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis (pages 6-8, Attachment II). A chain of custody sheet will accompany all samples. Sample flow rates will be calibrated prior to and after sampling in the field.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and various ELB Instrument Technicians.

VI. Travel/Monitoring Schedule

For each week of sampling, an Instrument Technician will travel to Imperial County on Sunday afternoon or Monday morning. Sampling will begin as early as possible Monday. The resin will be collected each day and replaced with fresh resin. On Friday morning the last samples will be collected. All

samples will be packed for shipment to the University of California, Davis and delivered to the shipping agent. The samples will be received by UC Davis staff on Saturday and properly stored until analysis.