

APPENDIX II  
LABORATORY REPORT

**Carbofuran in Air Samples Using XAD-4® Resin as a Trapping Medium**

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Disclaimer

The statements and conclusions in the report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

## ABSTRACT

Air sampling for carbofuran (2,3-Dihydro-2,2-dimethyl-benzofuran-7-yl methyl carbamate) was conducted from mid-February to mid-March at four ambient locations in Imperial County. An urban (background) site was established in the city of El Centro.

The samples were collected in air samplers charged with XAD-4 resin, as a sampling medium, and analyzed by a gas chromatographic method. The highest concentration of carbofuran was 2.1 micrograms ( $\mu\text{g}$ ) at the Imperial site. The site with the most positive samples was the Imperial site with 9 positive out of a total of 12 samples taken at this site. The average of all positive samples at this site was 0.84  $\mu\text{g}$ .

Several samples that had positive "hits" for carbofuran were confirmed by GC/MSD.

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## INTRODUCTION

Carbofuran, 2,3-Dihydro-2,2-dimethyl-benzofuran-7-yl methyl carbamate, CAS number: 1563-66-2, figure 1), is a systemic broad spectrum insecticide and nematocide with approximately 316,183 pounds applied in the State of California during 1992 (References 1,2). The major use of carbofuran in 1992, was on alfalfa for the control of weevils. Approximately one fourth of the total was applied to rice for the control of water weevils. During February and March, Carbofuran is applied to alfalfa for control of weevil infestations. Carbofuran is most notably sold under the trade name of Furidan®.

The physicochemical properties of Carbofuran are listed in Table 1.

Figure 1. Structure of Carbofuran is:

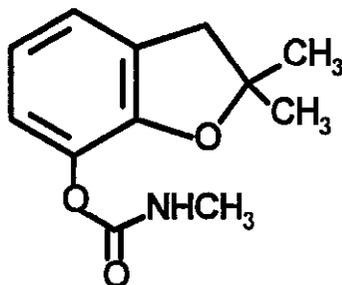


Table 1. Physicochemical Properties of Carbofuran

Chemical	Molecular Weight (g/mole)	Solubility (mg/l)	Vapor Pressure (kPa)	Log $K_{(ow)}$	Log $K_{(oc)}$	CAS Number
Carbofuran	221.3	700	0.867	1.3	1.6	1563-66-2

Air samples were taken three days a week from February 15 to February 24, 1995, ran four days a week from February 28 to March 10, 1995, under the jurisdiction of ARB personnel. The California Air Resources Board (CARB) set up five sites in Imperial County to monitor for ambient levels of carbofuran in air. Carbofuran residues were analyzed by The Department of Environmental Toxicology's Trace analytical Laboratory's (TAL) personnel.

## FIELD

### Field Sites

The ARB established five air sampling sites in Imperial county, near the town of El Centro in Southern California (Figure Two, Table Two). The sites and time of year were selected due to the proximity of agricultural growth and potential carbofuran use on alfalfa for the control of weevils. The sites included four ambient air sampling sites and an urban (background) site. The sampling apparatus consisted of motorized pump, tubing connected to Teflon® cups charged with XAD-4 resin. Samplers had average flow rates on the order of 15 lpm, while sampling durations were on the order of 24 hours. ARB personnel were responsible for all air sampling including set up, sampling procedures and sample shipment to the laboratory.

### Sample Storage and Shipment

All samples were kept on dry ice until the time of shipment. Samples were boxed, and placed in ice chests packed with dry ice and shipped at the end of the week (Friday) by Federal Express (FED EX) for overnight delivery to the FED EX terminal located at the Sacramento Metropolitan Airport where TAL personnel pick up the samples on Saturday morning. The exception was that the last week samples taken from March 7 to March 10 and shipped on March 11 were inadvertently shipped by FED EX to Memphis and did not arrive at TAL until March 13, 48 hours later than the anticipated arrival time.

### Field Spikes/Storage Stability Samples

Prior to the initial start of the field phase of the project, XAD-4 resin, 30 ml each, was fortified either with 1 or 10 µg of carbofuran, four replicates each, by TAL personnel and picked up on February 3, 1995 by ARB personnel. The spiked resin was transported to the field site then packed in dry ice and shipped back to the TAL lab six days later via FED EX, where these samples were extracted, worked up and analyzed immediately. The results are in Table 4 of the results section of this report.

Figure 2. Sample Site Locations in Imperial County

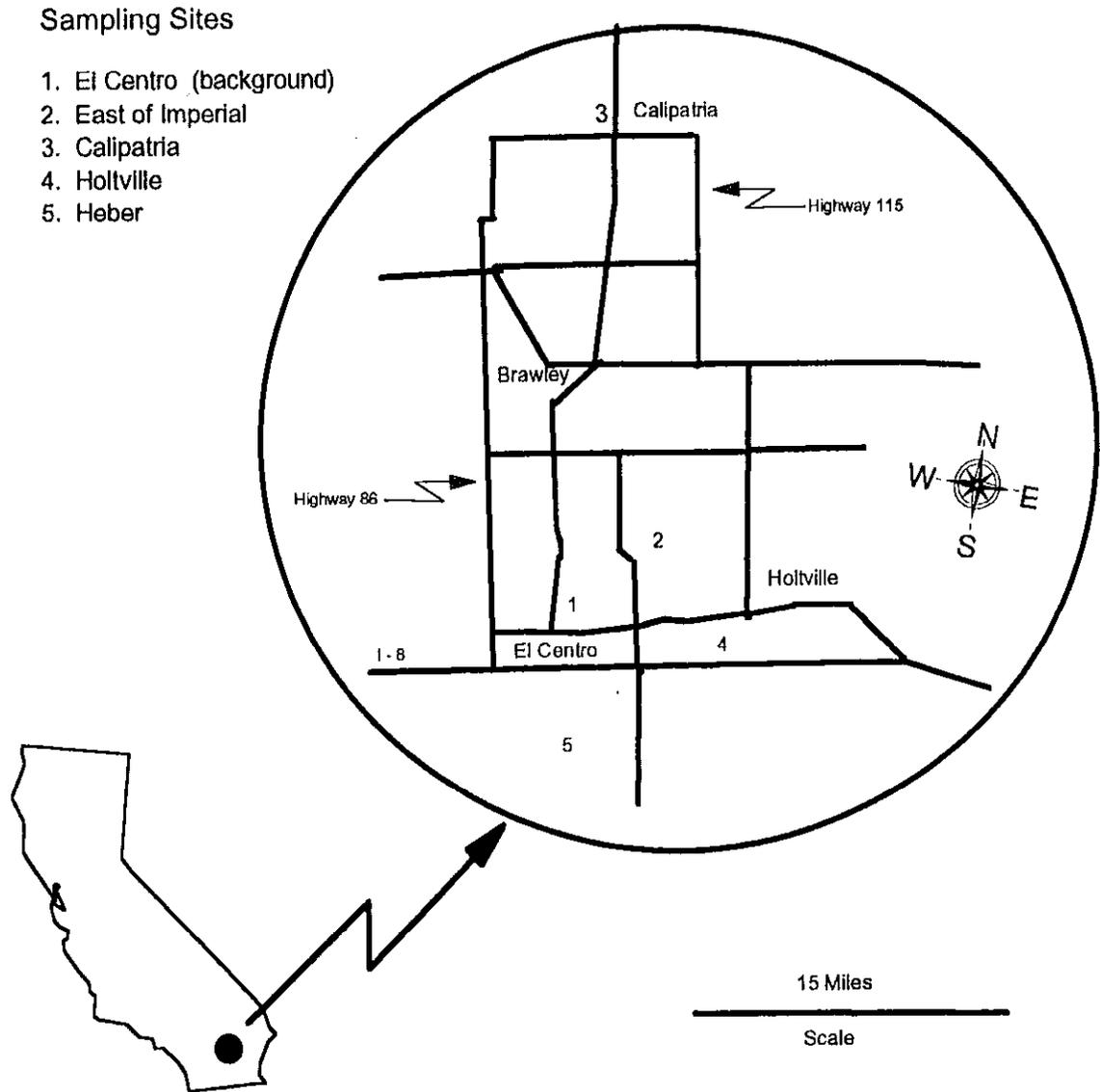


Table 2. Site locations

City	Location	Type	Sampler Location	Location ID
El Centro	Ag Commissioner	Urban Background	Roof	EC
Imperial	Air Pollution Control District PM10 Site	Ambient	Fenced Area	PM
Calipatria	Fire Station	Ambient	Roof	C
Holtville	Meadows Union School	Ambient	Roof	M
Heber	Felipe & Ramon Primary School	Ambient	Roof	H

## LABORATORY

### Material and Methods

Upon arrival at the laboratory, samples were inventoried, Chain of Custodies checked, and sample ID's logged into a Excel® spreadsheet. Sample work up began within one half hour of arriving at the laboratory.

### Analytical Standard

Carbofuran standard was purchased from Chem Service (Catalog # F2006, Lot# 121-104B, Purity: 99.0%, Expiration date: 2/97, Invoice# CS138769) was on Received 2/7/95 and were logged into in TAL's analytical standard repository. Neat standards were kept at -20 °C until the time of use. Stock solutions, 100 ml each, 1.0 mg/ml concentrations, were prepared and kept at 4 °C until the time of use. Dilute spiking and analysis standards were prepared from the stock solution. Fresh analytical standards were prepared as needed.

### Analytical Method

The original method used for the analysis of carbofuran was reported in a prior report to the ARB (Appendix B and Reference 4). Essentially, the method consisted of adding 75 ml of ethyl acetate to the resin and mechanically swirling for one hour and taking an aliquot of solvent (37.5 ml) The solvent was evaporated off and quantitatively transferred to sedimentation tubes and the final volume adjusted to 2 ml for analysis.

### Method Modifications

The first set of ambient air samples from Imperial County had interferences that required a clean up step after extraction and the transfer of 37.5 ml of solvent to a 100 ml round bottom flask. The clean up step included the follow procedure: The solvent was evaporated from each sample, taken up in ca 5 ml of hexane and added to a 9.5 cm X 1.5 cm (o. d.) with a 9.0 x 5.0 cm reservoir glass column that was packed with 3 centimeters of Florisil® and capped with 1 cm anhydrous sodium sulfate. The sample washed with 2 x 10 ml hexane followed by 25 ml of 5 percent ethyl acetate/hexane, which was discarded. Carbofuran was eluted from the column into a 100 ml round bottom flask with 45 ml of 15 percent ethyl acetate/hexane solution. The original method continued at this point (transfer and adjust total volume for analysis).

A schematic of the complete method used for these samples is shown in Figure 2.

All samples that were received each week were extracted, cleaned up and analyzed as a complete set. Laboratory spikes of XAD resin, 1.0 µg each, in triplicate, were run with

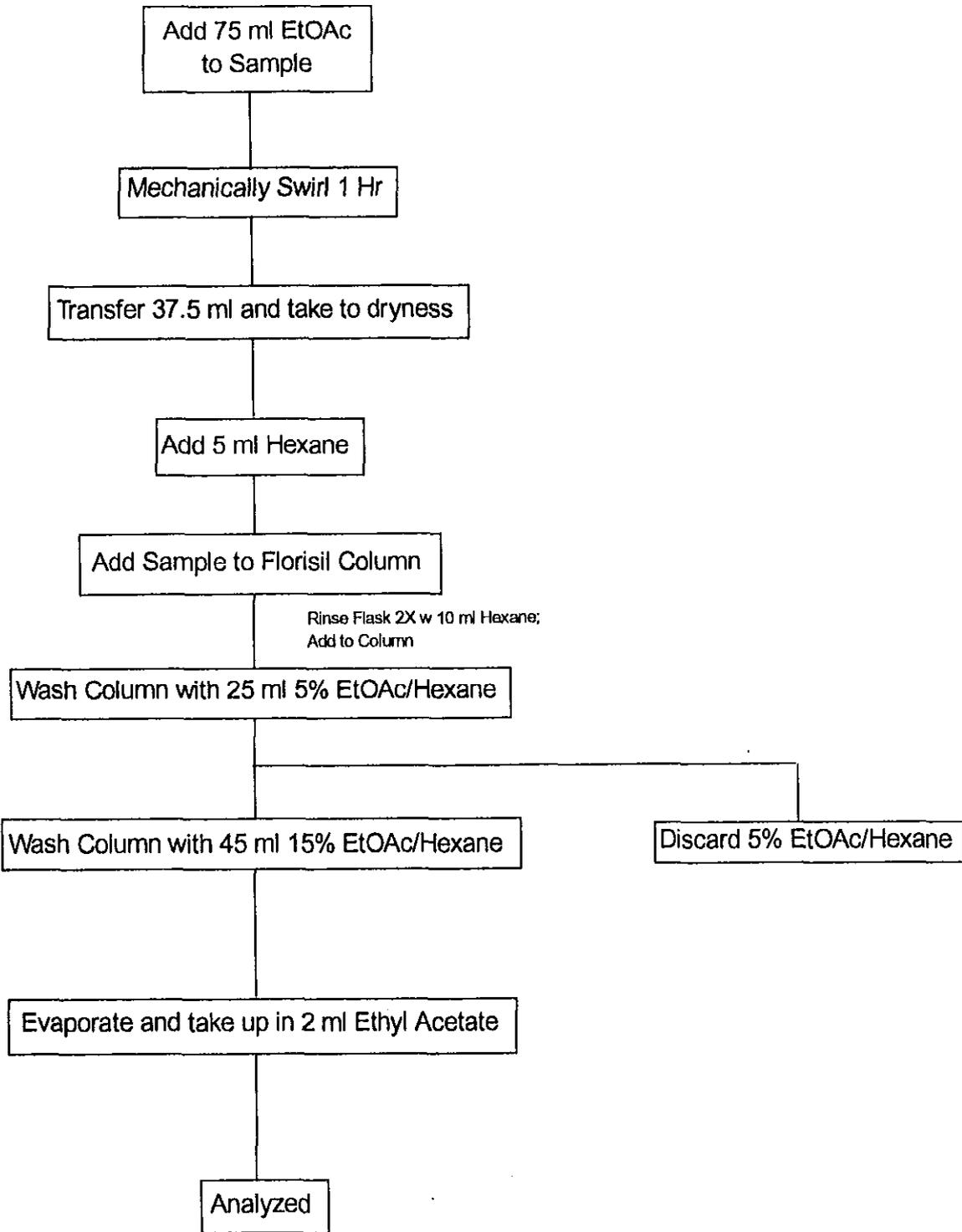
the each set of samples. The number of spikes were increased during the fourth week for the purposes of checking the clean up procedure. The results of these laboratory spikes are given in Table 7 of the results section.

### Problems and Issues

Upon receipt of the mis-shipped samples, samples dated March 7 - March 10, TAL personnel carefully inspected the ice chest. After the ice chest was open, all samples were inspected as to their temperature. There appeared to be small amounts of dry ice present and the samples felt cold to the touch. Two thermometers were placed at two different points inside the box that the air samples were packed in, and those temperatures were recorded. The average temperature inside the box was 6 °C, slightly above the normal temperatures found inside refrigerators. Because of the trace presence of dry ice and the box temperature appeared to be near that of a refrigerator, samples were worked up in the normal manner. To ensure that these samples were valid samples, three 1.0 µg fortified XAD-4 resin samples were placed on the lab bench at room temperature for two days to simulate the potential "worse case" of degradation. These samples were worked up and analyzed in the normal way. The results of these samples are given in the result section.

Three or four of the samples had labels that did not match the chain of custody and TAL personnel had to get clarification from ARB.

Figure 3. Method Schematic for Carbofuran



## Analysis

Two gas chromatographic systems were utilized for this project. System A, was a Perkin-Elmer Autosystem model gas chromatograph equipped with a nitrogen-phosphorous (N/P) detector and autosampler was used to quantitate carbofuran. The column used was a 0.53 mm (i.d.) X 30 m DB-5 Megabore<sup>®</sup> capillary column (J and W Scientific). A second equivalent system, System B, was used and consisted of a Hewlett Packard 5890A gas chromatograph with a N/P detector and a GC Autosampler. The bead voltage was adjusted to provide a minimum detectable of a 3  $\mu$ l injection of a 62.5 pg/ $\mu$ l standard. Peak quantitation accomplished via a TurboChrom<sup>®</sup> data station (Perkin Elmer) into an IBM<sup>®</sup> PC where the peaks were integrated and the results were entered into an EXCEL<sup>®</sup> (Microsoft) spreadsheet program and data reduction was performed using a macro. Parameters for the analytical instrumentation are listed in Table 3

Table 3. Gas Chromatograph Instrument Parameters

Instrument	Injector (C)	Detector (°C)	Temperature Column (°C)				Column
			Initial	Rate	Final	Hold (Min)	
System A	225	280	170	10	220	0	15 m x 0.53 mm DB-5MS <sup>1</sup> @ 5 ml/min
System B	250	280	170	10	240	3	30 m x 0.53 mm XTI-5 <sup>2</sup> @ 20 ml/min

1: J & W Scientific

2: Restek Inc.

## Quality Assurance

While it was not a requirement to follow strict Good Laboratory Practices (GLP) guidelines, quality assurance was kept at a maximum to keep the integrity of the project. Controls, (checks, blanks) and fortifications, three replicates of control resin fortified with 1.0  $\mu$ g each carbofuran, were run with every set. Documentation for the project was at a maximum, including the use of notebooks, instrument logbooks and/or computer spreadsheets. All of the necessary components were in place to assure that the study would be reconstructible, a prime requisite for a GLP study.

ARB quality assurance resin spikes were also analyzed as well as field spikes, resin samples that were fortified in the lab, taken to the sampling location for six days, brought back to the lab and analyzed.

Analysis of samples was quantified by using a 4-point external linear regression

standard curve for carbofuran that ranged from a maximum of 0.50 ng/ $\mu$ l to a minimum of 0.0625 ng/ $\mu$ l. Each sample was injected twice and standard(s) were interdispersed between samples during each analysis (set). The average of both analyses were reported.

#### Confirmation

Several samples, which gave a positive response for the nitrogen-phosphorus detector, and had the same retention time as carbofuran, were confirmed using a Hewlett Packard 5971A Mass Selective Detector (MSD), that was operated in the Selective Ion Monitoring mode (SIM), using ions 164 and 221 for confirming the presence of carbofuran in samples. The column was a 10 m X 0.25 mm DB - 5 narrow bore fused silica capillary column (J & W Scientific) that was operated at an initial temperature of 100 for 2 minutes and ramped to 160 at 10 °C/min and then ramped to 250 °C at 20 °C/min. The criteria used for confirmation was retention time with carbofuran standard comparison, plus the ratio of 164 ion to the 221 ion. Several samples were quantitated as well, using the MSD with the same standards used for the analytical method as a comparison.

#### Storage Stability

Storage stability data and procedures for carbofuran were done prior to the start of this phase of the project and were reported in a prior report to the ARB. Data from that report is included in Appendix B.

## RESULTS

A complete project history pertaining to this segment of the project, ambient air sampling in Imperial County, is given in Appendix A. Results of the prior segment, the Field Application Section, completed in April, 1993, is given in Appendix C. Also included in Appendix C, are the ARB quality assurance spikes for that time period.

### Field Spikes/Storage Stability

The results of the field spikes/storage Stability are given in Table 4. The four 1.0- $\mu\text{g}$  spikes ranged from 107% to 122% recovery with an average of 111% and a standard deviation of 7.9%. The 10  $\mu\text{g}$  resin spikes ranged from 99% to 104% with an average of 102% and a standard deviation of 2.2%.

Table 4. Field Spike/Storage Stability Recoveries

Spike Level	Replicate (%)				Average (%)	Standard Deviation
	1	2	3	4		
1.0 $\mu\text{g}$	112	107	104	122	111	7.9
10.0 $\mu\text{g}$	104	103	99	101	102	2.2

### Field Site Results

#### Analytical

The results for each of the sites is given in Table 5 and in Figure 4. The highest amount carbofuran found was 2.1  $\mu\text{g}$  at the PM (east of the town of Imperial) site on 2/24/95. The PM site also had the most positive hits with 9 out of 12 samples having amounts of carbofuran above the limit of detection ( $<0.25 \mu\text{g}/\text{sample}$ ). The site at M (Meadows Union School, Holtville) had 8 positive samples out of a total of 14 samples. The highest concentration at site M was 0.54  $\mu\text{g}$  on 3/9/95.

Only one of the two collocated samplers at Calipatria and one of the background site samples had a positive above the limit of detection which were 0.64 and 0.28  $\mu\text{g}$ , respectively. Because of the relatively low molecular weight and relatively high vapor pressure, it is reasonable to expect carbofuran detected at the El Centro site. Molinate, a rice herbicide with a similar molecular weight, has been shown to transport, in the vapor phase, for several miles (Reference 5). Furthermore, it has long been established that pesticides in air can transport for long distances (Reference 6).

Table 5. Carbofuran Results for Imperial County Sites ( $\mu\text{g}/\text{Sample}$ )

Date	C1 <sup>1</sup>	C2 <sup>1</sup>	PM <sup>2</sup>	M <sup>3</sup>	H <sup>4</sup>	EC <sup>5</sup>	B <sup>6</sup>
2/15/95	0.64	<0.25	0.28	0.48	<0.25	<0.25	<0.25
2/16/95	<0.25	<0.25	A	<0.25	<0.25	<0.25	<0.25
2/17/95	<0.25	<0.25	A	<0.25	<0.25	<0.25	<0.25
2/22/95	<0.25	<0.25	1.64	0.48	<0.25	<0.25	<0.25
2/23/95	<0.25	<0.25	1.59	0.27	<0.25	<0.25	<0.25
2/24/95	<0.25	<0.25	2.14	0.34	<0.25	0.28	<0.25
2/28/95	<0.25	<0.25	0.52	0.30	<0.25	<0.25	<0.25
3/1/95	<0.25	<0.25	0.37	0.34	<0.25	<0.25	<0.25
3/2/95	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
3/3/95	<0.25	<0.25	0.35	<0.25	<0.25	<0.25	<0.25
3/7/95	<0.25	<0.25	<0.25	T	<0.25	<0.25	<0.25
3/8/95	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
3/9/95	<0.25	<0.25	0.30	0.54	<0.25	<0.25	<0.25
3/10/95	<0.25	<0.25	0.34	0.36	T	<0.25	<0.25

1: Sampling Site: Ambient at Calipatria

2: Sampling Site: Ambient at PM10 Site East of Imperial

3: Sampling Site: Ambient at Meadows Union School, Holtville

4: Sampling Site: Ambient at Felipe & Ramon Primary School, Heber

5: Sampling Site: Urban background at El Centro

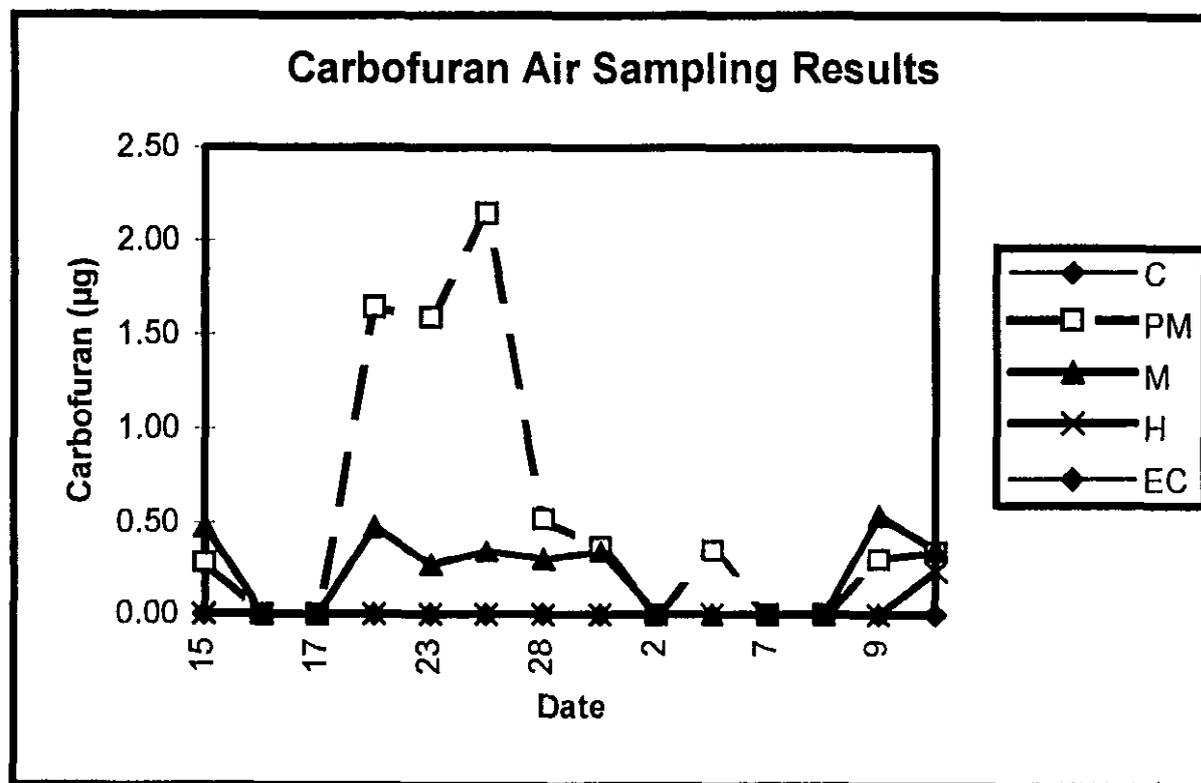
6: Blank resin that was taken to the field (field resin blank)

A: No sample received.

T: Trace (less than the limit of quantitation and above the limit of detection)

A complete listing of all of the samples, field resin banks and laboratory validation samples, in the order they were run, is given in Appendix E.

Figure 4. Carbofuran Air Sample Results



### Confirmation

Samples 4PM, 5PM, 6PM, from the PM10 monitoring site, east of Imperial, along with a laboratory validation sample, and 6B, a field blank site were confirmed using the MSD. These samples were also quantitated using the MSD. Table 6 gives the analytical results by nitrogen/phosphorus detection, mass selective detection and the percent difference between the two. It should be noted that neither the one positive sample from the background site nor the positive from the collocated site (Calipatria) were confirmed.

Table 6. Comparison of n/p and MSD Detectors

Sample ID	Carbofuran by n/p (µg)	Carbofuran by MSD (µg)	Difference	Percent Error <sup>1</sup>
6B (resin blank)	n. d.	n. d.	0.0	0.0
4 PM (Imperial)	1.6	1.7	-0.1	-6.3
5 PM (Imperial)	1.6	1.8	-0.2	-12
6 PM (Imperial)	2.1	2.4	-0.3	-14
5C2 (Calipatria)	n. d.	n. d.	0.0	0
1.0 µg Lab Spike	1.0	0.79	+0.21	+21

1: Percent Error = (N/p results - MSD results)/N/p results x 100

### Quality Assurance

All fortified XAD-4 resin laboratory validation samples gave excellent recoveries for carbofuran. The overall recovery for all validation samples was 98% with a standard deviation of 8.9 with n = 20. The results of all laboratory validation samples, listed by week, are given in Table 7. Validation spikes fortified then kept at room temperature for 48 hours are included in this table as well as cleanup column validation recoveries.

Table 7. Set Validation Results

	Replicate						Average	Standard Deviation
	1	2	3	4	5	6		
Week 1	80	103	111	---	---	---	98	16
Week 2	100	101	102	---	---	---	101	1.0
Week 3	89	94	94	---	---	---	92	2.9
Week 4	98	98	101	118 <sup>1</sup>	107 <sup>1</sup>	---	104	8.4
Week 5	86	91	85	97 <sup>2</sup>	100 <sup>2</sup>	98 <sup>2</sup>	93	6.4

1: Column cleanup recovery fortification

2: 1.0 µg Carbofuran at room temperature for 48 hours

Results of ARB's Quality Assurance audit samples are given in Table 8. According to ARB's Quality Assurance personnel, the results were acceptable. The results for 1993 and audit results for the application site phase may be found in Appendix C.

Table 8. ARB's QA Audit Samples (Total  $\mu\text{g}$  Found)<sup>1</sup>

Carbo 1	Carbo 2	Carbo 3	Carbo 4	Carbo 5	Carbo 6	Carbo 7
5.39	2.96	7.75	3.16	5.67	<0.25	8.72

1: Concurrent Laboratory Validation run with ARB's Audit spike samples 98%, 98% 101%; Average 99%.

### ACKNOWLEDGEMENTS

We wish to acknowledge the technical assistance of Lynn Baker, Ralph Propper, Don Fitzell and Ruth Tomlin with the California Air Resources Board, Matthew Hengel and Erica Kaneaiakala with the Department of Environmental Toxicology for their technical assistance. This study was supported by contract funds from the California Air Resources Board. Mention of proprietary products is made for identification purposes only and does not imply endorsement by ARB.

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6. *Long Range Transport of Pesticides*, David A. Kurtz, Ed., Lewis Publishers, Chelsea, MI,

## APPENDIX

### Appendix A: Project History

DATE	OBJECTIVE
1/15-1/31	Ordering solvents, glassware and misc. supplies.
2/2/95	Carbofuran spiking solutions and field spikes/storage stability samples
2/3/95	ARB personnel pick up field spikes/storage stability samples and transport them to the vicinity of Imperial County.
2/7/95	Received new carbofuran analytical standard. Stock mg/ml and analytical gas chromatography standards prepared.
2/9-2/11	ARB ships field spikes/storage stability samples to TAL Lab via FED EXPRESS. Samples extracted, worked up and analyzed upon arrival at TAL.
2/16/95	TAL personnel send proposed sampling methodology for carbofuran to ARB's QA unit.
2/18/95	Week One air samples arrive via FED EXPRESS. Sample extracted and worked up.
2/19-2/24	Week One air samples are analyzed. Interferences were noted and clean up procedure devised. Samples were run through clean up procedure and reanalyzed.
2/25/95	Week Two air samples arrive via FED EXPRESS. Samples extracted and worked up and analyzed.
2/28-3/5	Confirmation work pursued using a H-P mass selective detector in selective ion monitoring mode. Instrument parameters optimized, samples included ARB background site, sites with high response, laboratory spikes.
3/4-3/8	Third week samples pick up at FED EXPRESS and work up on 3/4/95. Samples analyzed and data reviewed 3/5/95-3/8/95.
3/10/95	Quality Assurance samples received from ARB's QA unit. Samples

Appendix A Continued

extracted upon delivery and analyzed with laboratory validation samples.

3/13/95 Results of ARB's quality assurance samples FAXED to ARB's QA unit.

3/15-4/15 Data checked, draft and final report written.

**Note:** Not part of this reporting period, but included in this segment of the project, is 3 weeks of resin preparation (8/5/94 to 8/26/94).

### Appendix B: Original Method and Freezer Stability Studies

The data in this appendix was originally reported to the ARB in 1993 by TAL personnel and is include for reference only.

Nineteen wide mouth screw-top glass jars, 5 cm diameter x 8.5 cm high were prepared by adding 30 ml of XAD-4 resin to each jar. One-hundred microliters each of carbofuran (1.00 mg/ml in ethyl acetate) was added to the resin in jars 1, 2 and 3 using a 100 µl Hamilton syringe. Similarly, 100 µl of 0.1 mg/ml was added to 4, 5, 6, and 100 µl each of 0.01 mg/ml were added to 7, 8 and 9. One jar was used as a control. The solvent was allowed to evaporate, the jars capped and placed in a freezer at -20°C for twelve days. The jars were removed and allowed to come to room temperature. Eighty milliliters of ethyl acetate was added to each jar, capped and extracted on a rotating platform for a minimum of 30 min. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results in Tables III reflect no degradation of the compound over the twelve day interval and complete extraction from the resin, (>95%) in all cases.

Table 9. Carbofuran Freezer Recovery Study\*

Amount Spiked (µg)	Replicate			Ave %	
	1	2	3	Recovery	SEM
100	90.6	92.2	92.2	91.7	0.6
10	110.0	110.7	110.0	110.1	0.4
1	108.7	111.3	101.2	107.0	3.7
			102.9	3.2	

\*Note: <1% of carbofuran found in control samples at all spiked levels.

Appendix C: April 1993 Application Site Air Sample Results

California Air Resources Board  
 Carbofuran Air Samples, 4/93  
 ARB Job# C93-013A

Table 10. 1993 Carbofuran Application Site Air Sampling Results

ARB Log #	ARB I	Total $\mu$ g
6	ON-1	<0.3
7	ON-2	<0.3
8	OE	<0.3
9	OS	<0.3
10	OW	<0.3
11	1N-1	<0.3
12	1N-2	<0.3
13	1E	0.9
14	1S	<0.3
15	1W	0.3
16	2W	1.3
17	2N-1	0.9
18	2N-2	0.6
19	2E	0.4
20	2S	<0.3
21	2B	<0.3
22	3W	1.8
23	3N-1	1.9
24	3N-2	2.3
25	3E	0.9
26	3S	<0.3
27	4W	0.9
28	4N-1	0.7
29	4N-2	0.7
30	4E	0.5
31	4S	<0.3
32	5W	0.3
33	5N-1	0.7
34	5N-2	0.8
35	5E	2.0
36	5S	1.1
37	6W	0.8
38	6N-1	1.3
39	6N-2	1.3
40	6E	2.6
41	6S	1.0
42	6B	<0.3

## Appendix C Continued

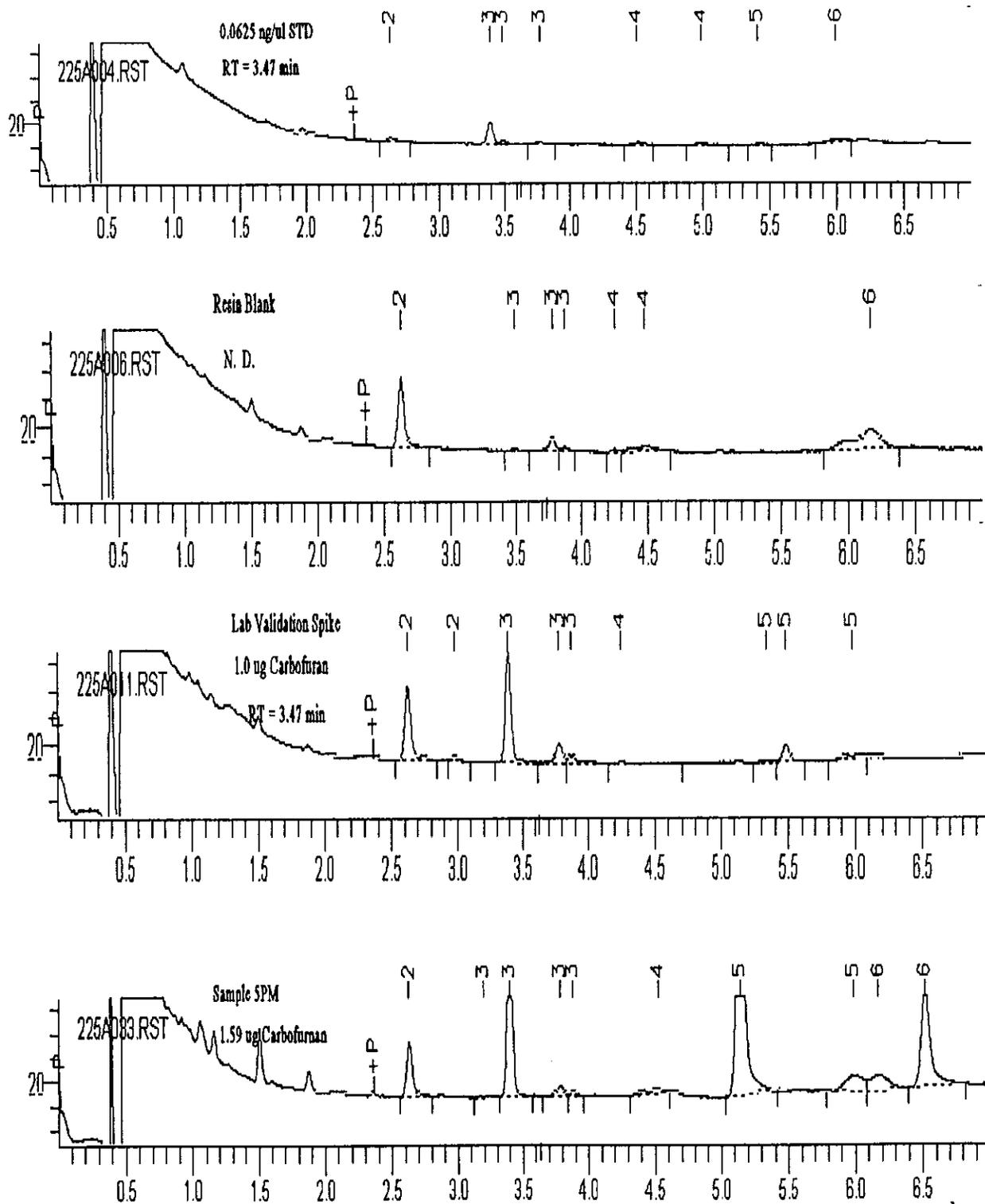
## ARB's QA Audit Spiked Resin Sample Results for April 1993 Field Application Project

Table 11. ARB Audit Spike Results for 1993 Carbofuran Field Application

ARB ID	Carbofuran ( $\mu\text{g}$ )		
CBF-1	4.8		
CBF-2	3.2		
CBF-3	9.4		
CBF-4	2.8		
CBF-5	<0.3		
CBF-6	4.5		
CBF-7	9.7		
AR I	0.98 $\mu\text{g}$	98%	
AR II	0.97 $\mu\text{g}$	97%	
AR III	0.90 $\mu\text{g}$	90%	
	average = 95%	$\pm$ 3 SEM	

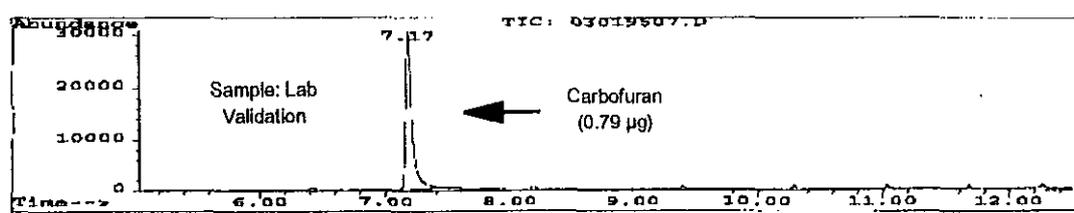
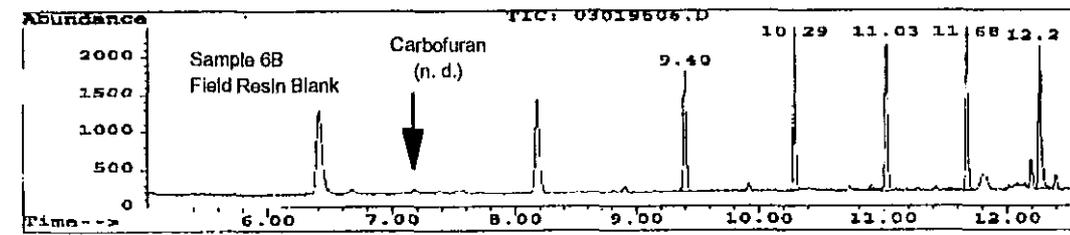
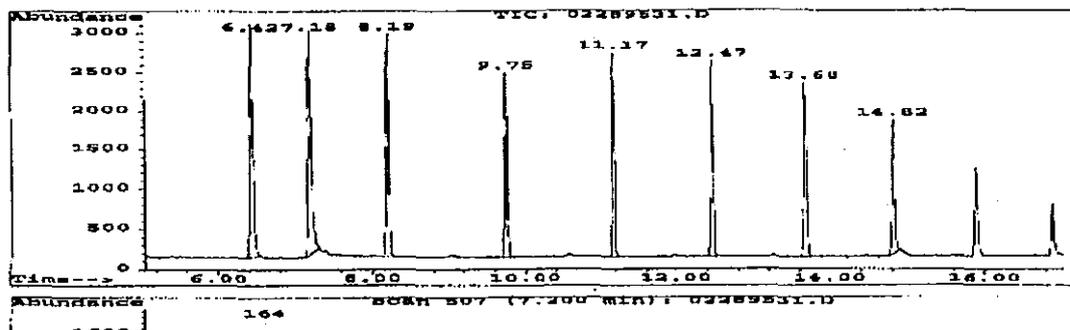
Appendix D. Chromatograms for Analytical and Confirmatory Methods

Figure 5. Analytical Chromatograms

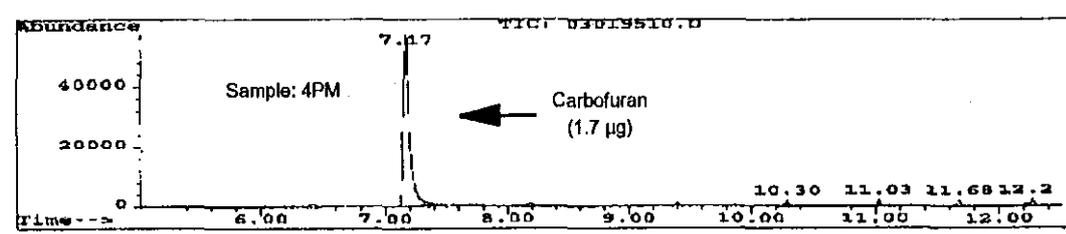


Appendix D Continued

Figure 6. GC/MSD Confirmation of Carbofuran



Ret Time	Signal Descr	Area	% Pk	%LPk
7.174	TIC	1110234	100.000	100.000



Ret Time	Signal Descr	Area	% Pk	%LPk
7.170	TIC	2119726	100.000	100.000
7.174	TIC	24524	100.000	100.000

## Appendix E: Laboratory Sample History and Individual Results

## Carbofuran in Air, ARB Project

Start Date: 2/11/95

Freezer Storage Location	Sample Log Number	Sample ID	Date Received	Date Collected	Date Extracted	Date Analyzed	Results ( $\mu\text{g}$ )	% Rec
D1	1	1C1	2/18/95	2/15/95	2/18/95	2/24/95	<b>0.64</b>	
D1	2	1C2	2/18/95	2/15/95	2/18/95	2/24/95	<0.25	
D1	3	1M	2/18/95	2/15/95	2/18/95	2/24/95	<b>0.48</b>	
D1	4	1EC	2/18/95	2/15/95	2/18/95	2/24/95	<0.25	
D1	5	1H	2/18/95	2/15/95	2/18/95	2/24/95	<0.25	
D1	6	1PM	2/18/95	2/15/95	2/18/95	2/24/95	<b>0.28</b>	
D1	7	2C1	2/18/95	2/16/95	2/18/95	2/24/95	<0.25	
D1	8	2C2	2/18/95	2/16/95	2/18/95	2/24/95	<0.25	
D1	9	2M	2/18/95	2/16/95	2/18/95	2/24/95	<0.25	
D1	10	2EC	2/18/95	2/17/95	2/18/95	2/24/95	<0.25	
D1	11	2H	2/18/95	2/16/95	2/18/95	2/24/95	<0.25	
D1	14	3C1	2/18/95	2/17/95	2/18/95	2/24/95	<0.25	
D1	15	3C2	2/18/95	2/17/95	2/18/95	2/24/95	<0.25	
D1	16	3M	2/18/95	2/17/95	2/18/95	2/24/95	<0.25	
D1	17	3EC	2/18/95	2/17/95	2/18/95	2/24/95	<0.25	
D1	18	3H	2/18/95	2/17/95	2/18/95	2/24/95	<0.25	
D1	13	2B	2/18/95	2/15/95	2/18/95	2/24/95	<0.25	
D1		V1.0R1	2/18/95	2/18/95	2/18/95	2/23/95	0.80	80%
D1		V1.0R2	2/18/95	2/18/95	2/18/95	2/23/95	1.03	103%
D1		V1.0R3	2/18/95	2/18/95	2/18/95	2/23/95	1.11	111%
D1	19	4C1	2/25/95	2/22/95	2/25/95	2/25/95	<0.25	
D1	20	4C2	2/25/95	2/22/95	2/25/95	2/25/95	<0.25	
D1	21	4PM	2/25/95	2/22/95	2/25/95	2/25/95	<b>1.64</b>	
D1	22	4M	2/25/95	2/22/95	2/25/95	2/25/95	<b>0.48</b>	
D1	23	4H	2/25/95	2/22/95	2/25/95	2/25/95	<0.25	
D1	24	4EC	2/25/95	2/22/95	2/25/95	2/25/95	<0.25	
D1	25	5C1	2/25/95	2/23/95	2/25/95	2/25/95	<0.25	
D1	26	5C2	2/25/95	2/23/95	2/25/95	2/25/95	<0.25	
D1	27	5PM	2/25/95	2/23/95	2/25/95	2/25/95	<b>1.59</b>	
D1	28	5M	2/25/95	2/23/95	2/25/95	2/25/95	<b>0.27</b>	
D1	29	5H	2/25/95	2/23/95	2/25/95	2/25/95	<0.25	
D1	30	54EC	2/25/95	2/23/95	2/25/95	2/25/95	<0.25	
D1	31	6C1	2/25/95	2/24/95	2/25/95	2/25/95	<0.25	
D1	32	6C2	2/25/95	2/24/95	2/25/95	2/25/95	<0.25	
D1	33	6PM	2/25/95	2/24/95	2/25/95	2/25/95	<b>2.14</b>	

Freezer Storage Location	Sample Log Number	Sample ID	Date Received	Date Collected	Date Extracted	Date Analyzed	Results (µg)	% Rec
D1	34	6 4M	2/25/95	2/24/95	2/25/95	2/25/95	<b>0.34</b>	
D1	35	6 4H	2/25/95	2/24/95	2/25/95	2/25/95	<0.25	
D1	36	6 4EC	2/25/95	2/24/95	2/25/95	2/25/95	<b>0.28</b>	
D1	37	6B	2/25/95	2/24/95	2/25/95	2/25/95	<0.25	
D1		V1.0R4	2/25/95	2/25/95	2/25/95	2/25/95	1.00	100%
D1		V1.0R5	2/25/95	2/25/95	2/25/95	2/25/95	1.01	101%
D1		V1.0R6	2/25/95	2/25/95	2/25/95	2/25/95	1.02	102%
D1	38	7C1	3/4/95	2/28/95	3/4/95	3/5/95	<0.25	
D1	39	7C2	3/4/95	2/28/95	3/4/95	3/5/95	<0.25	
D1	40	7PM	3/4/95	2/28/95	3/4/95	3/4/95	<b>0.52</b>	
D1	41	7M	3/4/95	2/28/95	3/4/95	3/4/95	<b>0.30</b>	
D1	42	7H	3/4/95	2/28/95	3/4/95	3/4/95	<0.25	
D1	43	7EC	3/4/95	2/28/95	3/4/95	3/4/95	<0.25	
D1	44	7B	3/4/95	2/28/95	3/4/95	3/4/95	<0.25	
D1	45	8C1	3/4/95	3/1/95	3/4/95	3/5/95	<0.25	
D1	46	8C2	3/4/95	3/1/95	3/4/95	3/5/95	<0.25	
D1	47	8PM	3/4/95	3/1/95	3/4/95	3/4/95	<b>0.37</b>	
D1	48	8M	3/4/95	3/1/95	3/4/95	3/4/95	<b>0.34</b>	
D1	49	8H	3/4/95	3/1/95	3/4/95	3/4/95	<0.25	
D1	50	8EC	3/4/95	3/1/95	3/4/95	3/4/95	<0.25	
D1	51	9C1	3/4/95	3/2/95	3/4/95	3/5/95	<0.25	
D1	52	9C2	3/4/95	3/2/95	3/4/95	3/5/95	<0.25	
D1	53	9PM	3/4/95	3/2/95	3/4/95	3/4/95	<0.25	
D1	54	9M	3/4/95	3/2/95	3/4/95	3/4/95	<0.25	
D1	55	9H	3/4/95	3/2/95	3/4/95	3/4/95	<0.25	
D1	56	9EC	3/4/95	3/2/95	3/4/95	3/4/95	<0.25	
D1	57	10C1	3/4/95	3/3/95	3/4/95	3/5/95	<0.25	
D1	58	10C2	3/4/95	3/3/95	3/4/95	3/5/95	<0.25	
D1	59	10PM	3/4/95	3/3/95	3/4/95	3/4/95	<b>0.35</b>	
D1	60	10M	3/4/95	3/3/95	3/4/95	3/4/95	<0.25	
D1	61	10 H	3/4/95	3/3/95	3/4/95	3/4/95	<0.25	
D1	62	10EC	3/4/95	3/3/95	3/4/95	3/5/95	<0.25	
D1		V1.0R7	3/4/95	3/4/95	3/4/95	3/4/95	0.89	89%
D1		V1.0R8	3/4/95	3/4/95	3/4/95	3/4/95	0.94	94%
D1		V1.0R9	3/4/95	3/4/95	3/4/95	3/4/95	0.94	94%
D1		Carbo 1	3/10/95		3/10/95	3/10/95	<b>5.39</b>	
D1		Carbo 2	3/10/95		3/10/95	3/10/95	<b>2.96</b>	
D1		Carbo 3	3/10/95		3/10/95	3/10/95	<b>7.75</b>	
D1		Carbo 4	3/10/95		3/10/95	3/10/95	<b>3.16</b>	

Freezer Storage Location	Sample Log Number	Sample ID	Date Received	Date Collected	Date Extracted	Date Analyzed	Results ( $\mu\text{g}$ )	% Rec
D1		Carbo 5	3/10/95		3/10/95	3/10/95	<b>5.67</b>	
D1		Carbo 6	3/10/95		3/10/95	3/10/95	<0.25	
D1		Carbo 7	3/10/95		3/10/95	3/10/95	<b>8.72</b>	
D1		V1.0R10	3/10/95	3/10/95	3/10/95	3/10/95	0.98	98%
D1		V1.0R11	3/10/95	3/10/95	3/10/95	3/10/95	0.98	98%
D1		V1.0R12	3/10/95	3/10/95	3/10/95	3/10/95	1.01	101%
D1		V1.0R13	3/10/95	3/10/95	3/10/95	3/10/95	1.18	118%
D1		V1.0R14	3/10/95	3/10/95	3/10/95	3/10/95	1.07	107%
D1	63	11C1	3/13/95	3/7/95	3/13/95	3/13/95	<0.25	
D1	64	11C2	3/13/95	3/7/95	3/13/95	3/13/95	<0.25	
D1	65	11PM	3/13/95	3/7/95	3/13/95	3/13/95	<0.25	
D1	66	11M	3/13/95	3/7/95	3/13/95	3/13/95	T	
D1	67	11H	3/13/95	3/7/95	3/13/95	3/13/95	<0.25	
D1	68	11EC	3/13/95	3/7/95	3/13/95	3/13/95	<0.25	
D1	69	11B	3/13/95	3/7/95	3/13/95	3/13/95	<0.25	
D1	70	12C1	3/13/95	3/8/95	3/13/95	3/13/95	<0.25	
D1	71	12C2	3/13/95	3/8/95	3/13/95	3/13/95	<0.25	
D1	72	12PM	3/13/95	3/8/95	3/13/95	3/13/95	<0.25	
D1	73	12M	3/13/95	3/8/95	3/13/95	3/13/95	<0.25	
D1	74	12H	3/13/95	3/8/95	3/13/95	3/13/95	<0.25	
D1	75	12EC	3/13/95	3/8/95	3/13/95	3/13/95	<0.25	
D1	76	13C1	3/13/95	3/9/95	3/13/95	3/13/95	<0.25	
D1	77	13C2	3/13/95	3/9/95	3/13/95	3/13/95	<0.25	
D1	78	13PM	3/13/95	3/9/95	3/13/95	3/13/95	<b>0.30</b>	
D1	79	13M	3/13/95	3/9/95	3/13/95	3/13/95	<b>0.54</b>	
D1	80	13H	3/13/95	3/9/95	3/13/95	3/13/95	<0.25	
D1	81	13EC	3/13/95	3/9/95	3/13/95	3/13/95	<0.25	
D1	82	14C1	3/13/95	3/10/95	3/13/95	3/13/95	<0.25	
D1	83	14C2	3/13/95	3/10/95	3/13/95	3/13/95	<0.25	
D1	84	14PM	3/13/95	3/10/95	3/13/95	3/13/95	<b>0.34</b>	
D1	85	14M	3/13/95	3/10/95	3/13/95	3/13/95	<b>0.36</b>	
D1	86	14H	3/13/95	3/10/95	3/13/95	3/13/95	T	
D1	87	14EC	3/13/95	3/10/95	3/13/95	3/13/95	<0.25	
D1		V1.0R15	3/13/95	3/13/95	3/13/95	3/13/95	0.86	86%
D1		V1.0R16	3/13/95	3/13/95	3/13/95	3/13/95	0.91	91%
D1		V1.0R17	3/13/95	3/13/95	3/13/95	3/13/95	0.85	85%
D1		V1.0R18	3/14/95	3/14/95	3/16/95	3/16/96	0.97	97%
D1		V1.0R19	3/14/95	3/14/95	3/16/96	3/16/96	1.00	100%
D1		V1.0R20	3/14/95	3/14/95	3/16/96	3/16/96	0.98	98%