CONTRACT NO. 92-314
FINAL REPORT
DECEMBER 1993

Pilot Monitoring Study of Two Pesticides in Air

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

Pilot Monitoring Study of Two Pesticides in Air

Final Report

Contract No. 92-314

Prepared for:

California Air Resources Board
Research Division
2020 L Street
Sacramento, California 95814

Prepared by:

Takayuki Shibamoto
Chuck Mourer
and
Gregory Hall

Department of Environmental Toxicology
University of California, Davis
Davis, California 95616

December 1993

Acknowledgments

The authors of this report acknowledge the valuable assistance provided by the staff of the Air Resources Board, particularly Ralph Propper, Lynn Baker, Ruth Tomlin, and Don Fitzell.

This project was submitted in fulfillment of ARB Contract No. 92-314, Pilot Monitoring Study of Two Pesticides in Air, by the Trace Analytical Laboratory of the Department of Environmental Toxicology at U.C. Davis under the sponsorship of the California Air Resources Board. Work was completed as of August, 1993.

Disclaimer

Table of Contents

Overview

Introduction

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducts two types of pesticide air monitoring programs: 1) three-day source impacted ambient monitoring adjacent to a recently applied field (application monitoring), and 2) four-week ambient monitoring in population centers located in the vicinity of expected applications (ambient monitoring). As required by Food and Agricultural Code Section 14022, this monitoring is conducted to provide DPR with data for the evaluation of the persistence and public exposure of airborne pesticides.

For some pesticides there are no validated air sampling and analytical methods. Chapters 1 and 2 contain the research, conducted by the University of California Davis, Department of Environmental Toxicology, Trace Analytical Laboratory (TAL), on method development and validation for carbofuran and captan. This research enabled the ARB/EEB to collect samples and calculate ambient concentrations in the three monitoring studies described in this report (Appendices I, II, and III). The ARB Quality Assurance Section carried out audits of the flow rate of the air samplers used in the monitoring, and a system audit of the TAL to review sample handling and storage procedures, analytical methodology, and method validation (Appendices IV and V).

These studies were: an application monitoring for carbofuran (Appendix I), and ambient (Appendix II) and application (Appendix III) monitoring for captan and its breakdown product, tetrahydrophthalimide (THPI). All samples were collected by ARB/EEB and analyzed by the TAL.

The first study, of carbofuran applied by a ground rig as an insecticide on alfalfa, was conducted in March 1993, in Imperial County. This location was selected because the predominant use for carbofuran was on alfalfa, and the peak use is from February through March in Imperial County. In the second study, captan and THPI ambient monitoring was conducted in May in Kern County. The greatest amount of captan is applied during May in Kern County. The third study, of captan and THPI concentrations after a ground application of captan to grapes as a fungicide, was conducted in May in Tulare County.

Sampling Methodology

The sampling method used during these studies required passing measured quantities of ambient air through a bed of XAD-4 resin. The holder was made of Teflon and contained approximately 30 cc of resin. The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any captan or carbofuran present in the sampled air was captured by the XAD-4 adsorbent. Each sampling train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, train support, and an AC or DC powered vacuum pump. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight. Subsequent to sampling, the resin was transported on dry ice to U.C. Davis, for analysis.

Analytical Methodology

Prior to sampling in the field, a computer-aided literature search for air sampling and analytical methodology was done for the pesticides. The TAL identified the appropriate trapping media, XAD-4 resin, for the three compounds. Storage stability studies and validation of analytical methods were also carried out before sampling began.

Appropriate analytical methods were developed for the separation and quantitation of each target pesticide. A gas chromatograph instrument with a DB-5 megabore column followed by a nitrogen/phosphorous detector was primarily used. For certain captan samples, a Hall Electroconductivity Detector was used instead to enhance sensitivity and selectivity.

Results/Discussion

Carbofuran

Application monitoring for carbofuran was done in Imperial County from March 31 to April 2, 1993. Samplers were placed about 20 yards from each edge of a 70-acre rectangular field. Relatively low values were found, ranging from 0.03 to 0.66 $\mu g/m^3$ over the 44-hour sampling period. Samples of 1-2 hours in duration were taken following initiation of the application, and gradually increased to ten hours in duration the first day, followed by a final twenty-three hour sample. The highest level of 0.66 $\mu g/m^3$ was observed during a 1-hour sample downwind of the application, and in a 3-hour sample three hours after completion of the application (Appendix I). Carbofuran has a vapor pressure of 1.28E-06 mm Hg. Temperatures ranged from 50°F at night to 85°F during the day over the sampling period.

Captan

Ambient monitoring, consisting of 24-hour samples for captan and THPI, was conducted in Bakersfield and three towns southeast of Bakersfield, from May 11 through June 4, 1993. No samples were above the average minimum detection limits for the 24-hour samples of 0.013 $\mu g/m^3$ for captan, and 0.026 $\mu g/m^3$ for THPI (Appendix II).

Application monitoring for captan was done in Tulare County from May 24 to May 28, 1993, for a period of approximately seventy-two hours following application. Samplers were placed about 20 yards from each edge of an 18-acre rectangular field. Three of the only four positive captan samples were found in the first two and one-half hour sampling period following initiation of the application, and ranged from 0.28 to 0.47 $\mu g/m^3$, with the other positive sample of 0.03 $\mu g/m^3$ occurring during the second 12-hour period after application (Appendix III). The vapor pressure for captan is 8.00E-08 mm Hg. No THPI was detected above its limit of quantitation (0.50 μg/sample) in any of the samples. Temperatures ranged from 55 F^oat night to 85^{o}F during the day.

Recommendations

1. To the extent possible, field samples should be handled using the same conditions as the laboratory storage stability samples to ensure valid results.

2. Where feasible, the volume of air sampled should be maintained within a narrow range to assure a uniform limit of detection for all samples.

3. When sampling for short sampling periods (such as applications), the sampler flow should be maintained at the upper end of the flow range. This would allow either increasing the possibility of getting measurable residues, or determining a lower limit of detection.

4. Applications of compounds with low volatility could utilize high volume air samplers. This would lower the number of samples below the limit of detection while not overloading the collection system.

5. Field spikes of control/blank samples could be used to validate sample integrity, particularly where storage sample validation conditions could not be replicated in the field.

6. Where appropriate, response factor plots could be done to measure instrument stability.

Chapter 1 Carbofuran Application Monitoring Report (TAL)

Table of Contents

Analysis of the Insecticide, Carbofuran, in Air

The Department of Pesticide Regulation (DPR) has requested that the California Air Resources Board (ARB), as part of their toxic air contaminants program, determine airborne exposure to selected pesticides. Candidate pesticides for exposure analysis included carbofuran.

(1) Literature Search

A computer-aided literature search for air sampling and analytical methodology was done on the pesticide. The 950 references generated by the computer search of Chemical Abstracts were assessed for any applicable methodology. Files maintained in the laboratory were reviewed for pertinent methodological information. Notebooks on previous projects referenced by pesticide in the Trace Analytical Laboratory (TAL) were assessed. Files maintained by the Environmental Toxicology Documentation Center by pesticide were evaluated for relevant articles.

(2) Preliminary Gas Chromatography

The trapping efficiency, initial validation and freezer storage samples were analyzed using a Hewlett-Packard Model 5890 series II gas chromatograph equipped with a nitrogen-phosphorous detector and a Model 7673 autoinjector. The column was a "Megabore" 30 m x 0.53 mm ID DB-5. Flows for helium carrier, nitrogen makeup, air and hydrogen were, respectively, 10, 20, 120, 3 ml/min. The injector and detector temperatures were 280°C. The oven temperature program was 180°C initial with no hold, programmed to 240°C at 20°C/minute with a final hold of four minutes.

(3) Air Trapping Efficiencies

A high volume Staplex air sampler was run for 24 hours. The air sampler had a manifold with four pairs of sampling cups (see Figure I). Sampling cups were comprised of a 4.0 cm x 12.1 cm Teflon cartridge with caps, a 100 mesh stainless steel retainer screen, 30 ml of pre-cleaned (see resin preparation) XAD-4 macroreticular resin, a glass wool plug and a top cap. The sampling cups were assembled by: (1) pressing the 100 mesh stainless steel screen into one end of the cartridge as a retainer for the sampling medium, (2) attaching an end cap, (3) pouring the resin in at the other (inlet) end on top of the screen, (4) inserting a glass wool plug, and (5) attaching the inlet cartridge cap. Two sampling cartridges were connected together with Teflon tubing, inlet to outlet and a funnel securely attached to the top sampling cup inlet. The assembled sampling cup pair was then attached to the manifold tubing of the air pump by the outlet of the bottom sampling cup. Spiking was done by slowly adding 100 µl of 1.00 mg/ml solutions (in acetone) onto the funnel using a Hamilton syringe. Three sampling cup pairs on the air sampler were spiked with 100 µg each of carbofuran, and the fourth pair was an unspiked control. The air pump was started and the measured air flows at the funnel ranged from 48 to 67 liters/min (data not shown). After 24 hours of running, the sampling cups were disassembled. The funnels were washed repeatedly with ethyl acetate into a volumetric flask using a disposable pipette until a total of 50 ml was reached. The resin was poured into a 125 ml erlenmeyer flask, the corresponding glass wool added, the flask sealed and the sample extracted on a rotating platform for a minimum of 30 minutes. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. The results for the carbofuran in Table I indicated good trapping efficiency (>90%) with no measurable breakthrough to the back resin, and good recoveries (>90%).

Figure I

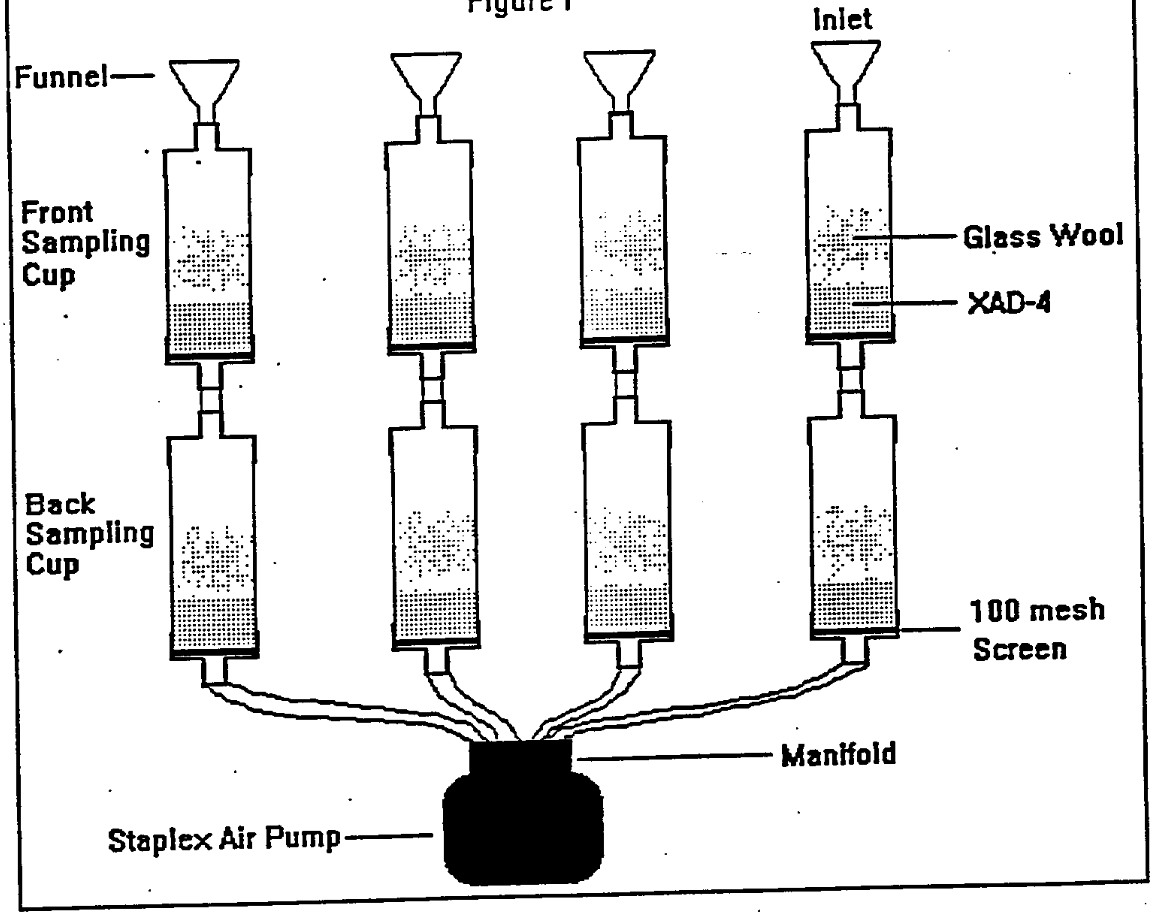


Table I, Carbofuran Trapping Efficiency Study, 100 µg Spike

% Recovery

Sample	Funnel	Front Resin	Back Resin	Total
Rep 1	60.9	36.0	<1	96.9%
Rep 2	45.3	50.4	<1	95.7%
Rep 3	56.0	38.4	<1	94.4%
Average =	54.1	41.6	<1	95.7%
SEM* =	5.6	5.5		0.9%
Control	<1	<1	<1	<3

Carbofuran% trapping efficiency = [41.6 x 100]/[100-54.1] = 90.6%

*Note: SEM = Standard Error of the Mean = square root((variance/(n-1

(4) Method Validation

Seven 125 ml erlenmeyer flasks were prepared by adding 30 ml of XAD-4 resin to each flask. One hundred microliters of carbofuran (1.00 mg/ml in ethyl acetate) was added to the resin in a pair of flasks using a 100 µl Hamilton syringe. Similarly, 100 µl of 0.1 mg/ml was added to second pair of flasks, and 100 µl of 0.01 mg/ml was added to a third pair. The seventh flask was used as a control. The solvent was allowed to evaporate, and 80 ml of ethyl acetate was added to each flask. The flasks were sealed and then placed on a rotating platform for a minimum of 30 minutes. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results shown in Tables II had good extraction recoveries (>95%) from the resin.

Table II, Carbofuran Method Validation Study*

Amount Spiked (µg)	Replicate 1	Replicate 2	Ave % Recovery	SEM
100	104.9	112.0	107.9	2.2
10	102.6	94.8	98.7	2.4
1	99.7	98.7	99.2	2.2
			101.5	1.6

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

(5) Freezer Stability Studies

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. T solvent was allowed to evaporate, the jars capped and placed in freezer at -20°C for twelve days. The jars were removed and allowed come to room temperature. Eighty mililiters of ethyl acetate was add to each jar, capped and extracted on a rotating platform for a minim of 30 min. The extracts were either analyzed directly or 40 evaporated to the appropriate volume and then analyzed by g chromatography. The carbofuran results in Tables III reflect degradation of the compound over the twelve day interval and comple extraction from the resin, (>95%) in all cases.

Table III, Carbofuran Freezer Recovery Study*

Amount Spiked (µg)	Replicate 1	Replicate 2	Replicate 3	Ave % 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 level

(6) XAD-4 Resin Preparation

1. A 61 x 29 cm cylindrical Pyrex container (approx. 40 l) was thoroughly cleaned with soap and water.
2. Sixteen liters of XAD-4 resin (see note) was added to the container.
3. One gallon of methanol (Resi-grade or equivalent) was added. The resin will expand in the presence of organic solvents. This prevented rapid expansion of the resin.
4. The container was filled with deionized (DI) water with the hose placed at the bottom of the container and stirred vigorously.

5. A vacuum apparatus was prepared with a stiff tube covered at the inlet end with gauze and the outlet end connected to a large trap.
6. As the resin settles, the "fines" were vacuumed-up. When the gauze became covered with "fines", they were wiped off and discarded.
7. The container was re-filled with DI water and stirred.
8. Steps #6 and 7 were repeated until the water above the resin was clear.
9. The pH of the water was checked (usually about 10 from the bicarbonate coating of the resin).
10. Two liters of 0.25 N hydrochloric acid were added and stirred for 30 minutes.
11. The pH of the water was checked and then as much water as possible was removed with vacuum.
12. If the pH was >5 (the pH of our DI water), then new water was added and steps 9 to 11 repeated (usually at least 10 times).
13. Add 1 gallon of methanol and let stand overnight.
14. Pour slurry back into empty solvent bottles.
15. Eight pairs of "knee high" nylons were extracted in the thimble of a Soxlet extractor using ethyl acetate as the extraction solvent. This removed the dye from the nylons.
16. One nylon was placed inside the second to form a double wall and both were stretched directly over a Soxlet extractor chamber.
17. The slurry of methanol/resin was poured (approx. 2 l) was full of resin to just below the side arm, and the nylon tied off.
18. The resin was extracted twice for 24 hours (each time replacing the solvent) with methanol and ethyl acetate (Resi-grade) for a total of 4 days.
19. The cylinder of nylon/resin was removed and the resin poured into a 21 cm x 21 cm rectangular pyrex dish.
20. The resin was dried in a vacuum oven (25") for 3-4 days at 65°C.
21. The resin was transferred to a clean glass bottle for storage.
Note: XAD-4 resin, Rohm-Hass & distributed by Supelco.

(7) Gas Chromatography

Analysis of the second set of validation samples, submitted air samples and quality assurance samples was accomplished with a Varian Model 6500 gas chromatograph equipped with a thermionic specific detector (N/P) and a Varian Vista Model 402 data system. The column was a "Megabore" 30 m x 0.53 mm ID DB-5. Flows for helium carrier, makeup, air and hydrogen were 12, 20, 175, 4.5 ml/min, respectively. Oven temperature program was 160°C initial with 2 minute hold, and programmed to 250°C at 10°C/minute with a final hold of one minute. This resulted in a total run time of 12 minutes. The retention time of carbofuran was 6.27 minutes.

(8) Method Validation

On 4/9/93, three unused prepared samples (30 mL of XAD-4 in a screw-top glass jar) were each fortified by adding 1.00 µg of carbofuran (1.00 ml of 1.00 ng/µl in ethyl acetate) slowly on top of the resin using a volumetric pipette. The solvent was allowed to evaporate, and 75 ml of ethyl acetate was added to each jar. The jars were capped and then placed on a rotating platform for a minimum of 30 minutes. The 35 ml of each extract was evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results are shown in Table IV and had good extraction recoveries (>90%) from the resin.

Table IV, Method validation Samples

Sample	µg Spiked	Total µg	% Recovery
AR I	1.00 µg	0.98 µg	98%
AR II	1.00 µg	0.97 µg	97%
AR III	1.00 µg	0.90 µg	90%
			average = 95% ± 3 SEM

(9) Submitted Air Samples

On 4/5/93, Jack Rogers delivered a total of 37 samples in an ice chest with "Blue Ice" bags. The samples were inspected, placed into a -20°C freezer and assigned unique TAL log numbers. The ARB log numbers for these samples were 6 to 42. On 4/9/93 (4 days from receipt) all samples were removed from the freezer and allowed to come to room temperature. Seventy-five ml of ethyl acetate was added to each jar. The jars were capped and then placed on a rotating platform for a minimum of 30 minutes. The 35 ml of each extract was evaporated to the appropriate volume and then analyzed by gas chromatography. The carbofuran results are shown in Table V. The limit of quantitation (LOQ) for carbofuran was established at <0.3 µg total per sample. The LOQ was defined at being five times the baseline noise. A calculation is:

<0.3 µg = (<0.20 ng/3 µl injected) x (2 ml final volume) x (75 ml orig vol/35 ml taken)

Table V, Submitted Air Samples

ARB Log #	ARB ID	Total µg
6	0N-1	<0.3
7	0N-2	<0.3
8	0E	<0.3
9	0S	<0.3
10	0W	<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

(10) Submitted Quality Assurance Samples

On 4/15/93, seven quality assurance samples were delivered by courier. These samples were immediately assigned TAL log numbers and analyzed. Seventy-five ml of ethyl acetate was added to each jar, and the samples were analyzed as in Section 4. The carbofuran results are shown in Table VI.

Table VI, Submitted Quality Assurance Samples

ARB Log #	ARB ID	Total µg
n/a	CBF-1	4.8
n/a	CBF-2	3.2
n/a	CBF-3	9.4
n/a	CBF-4	2.8
n/a	CBF-5	<0.3
n/a	CBF-6	4.5
n/a	CBF-7	9.7

Chapter 2 Captan Application and Ambient Monitoring Report (TAL)

Table of Contents

Analysis of the Fungicide, captan, and its breakdown product tetrahydrophthalimide, in air

The Department of Pesticide Regulation (DPR) has requested that the California Air Resources Board (ARB), as part of their toxic air contaminants program, determine airborne exposure to selected pesticides. Candidate pesticides for exposure analysis include captan (including the captan breakdown product, THPI).

(1) Literature Search

A computer-aided literature search for air sampling and analytical methodology was done on the pesticide. The 950 references generated by the computer search of Chemical Abstracts were assessed for any applicable methodology. Files maintained in the laboratory were reviewed for pertinent methodological information. Notebooks on previous projects referenced by pesticide in the Trace Analytical Laboratory (TAL) were assessed. Files maintained by the Environmental Toxicology Documentation Center by pesticide were evaluated for relevant articles.

(2) Preliminary Gas Chromatography

Captan and THPI trapping efficiency, initial validation and freezer samples were analyzed using a Hewlett-Packard Model 5890 series II gas chromatograph equipped with a nitrogen-phosphorous detector and a Model 7673 autoinjector. A "Megabore" DB-5 column, 30 m x 0.53 mm ID was used. Flows for helium carrier, nitrogen makeup, air and hydrogen were, respectively, 10, 20, 120, 3 ml/min. The injector and detector temperatures were 280°C. For captan the oven temperature program was 180°C initial with no hold, programmed to 240°C at 20°C/minute with a final hold of four minutes. For THPI the oven temperature program was 120°C initial with no hold, programmed to 180°C at 10°C/minute with a final hold of three minutes.

An alternate system occasionally was used to analyze captan samples. A Varian Model 6000 gas chromatograph equipped with a Tracor Model 700A Hall Electroconductivity Detector and a Varian Vista Model 402 data system. The column was a "Megabore" 30 m x 0.53 mm ID DB-1. Flows for helium carrier, helium makeup and hydrogen combustion gas were 10, 20 and 50 ml/minute, respectively. Injector, detector oven and combustion temperatures were 250, 280, and 850°C, respectively. For captan the oven temperature program was 170°C initial with no hold, programmed to 230°C at 10°C/minute with no final hold.

An alternate system was occasionally used to analyze THPI. A Varian Model 6000 gas chromatograph equipped with a thermionic specific detector (N/P) and a Varian Vista Model 402 data system. The column was a "Megabore" 30 m x 0.53 mm ID DB-5. Flows for helium carrier (including makeup), air and hydrogen were 25, 175, 4.5 ml/min, respectively. The oven temperature program was 120°C initial with no hold, programmed to 180°C at 10°C/minute with no final hold.

(3) Air Trapping Efficiencies

Two high volume Staplex air samplers were run for 24 hours. Each air sampler had a manifold with four sampling cup pairs (see Figure I). A front sampling cup was made by pressing a screen approximately 3 cm inside the cartridge, added 30 ml of XAD resin, a second screen place over the resin forming a "sandwich" and a cartridge cap attached to the outlet. A plug of glass wool was then placed partially into the inlet of the cup. A back sampling cup was made by preparing a "sandwich" as before, and a cap attached to the outlet and the inlet (without any glass wool). A front and back sampling cup pair was made with tubing as before. The assembled sampling cup pair was then attached to the manifold tubing of the air pump by the outlet of the bottom sampling cup. Spiking was done by slowly adding 100 μl of captan (100 μg) directly to the glass wool in three of the sampling cup pairs (Note: The solvent was allowed to evaporate before the pumps were started). The fourth pair was an unspiked control. In the same manner, THPI was added to three sampling cup pairs on the second Staplex air sampler. The fourth pair was an unspiked control. When the air pumps were started, the measured air flows ranged from 40 to 69 liters/min (data not shown). After 24 hours of running, the measured air flows remained essentially unchanged (data not shown). The sampling cups were disassembled. The glass wool plugs were placed in a 125 ml erlenmeyer containing 80 ml of ethyl acetate and sealed. For each sampling cup, the resin was poured into a 125 ml erlenmeyer. The sampling cartridge was washed with 80 ml of ethyl acetate into the erlenmeyer containing the resin, and the flask was sealed. All samples were extracted on a rotating platform for a minimum of 30 minutes. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. Captan results shown in Table I had good trapping efficiency (>90%) with no measurable breakthrough to the back resin, and good recoveries (>90%). Results for THPI in Table II had fair trapping efficiency (>50%) with no measurable breakthrough to the back resin, and fair recovery (>60%). The recovery data suggest that the trapping efficiency could be greater than indicated, possibly due to breakdown of the chemical during the test.

Figure I

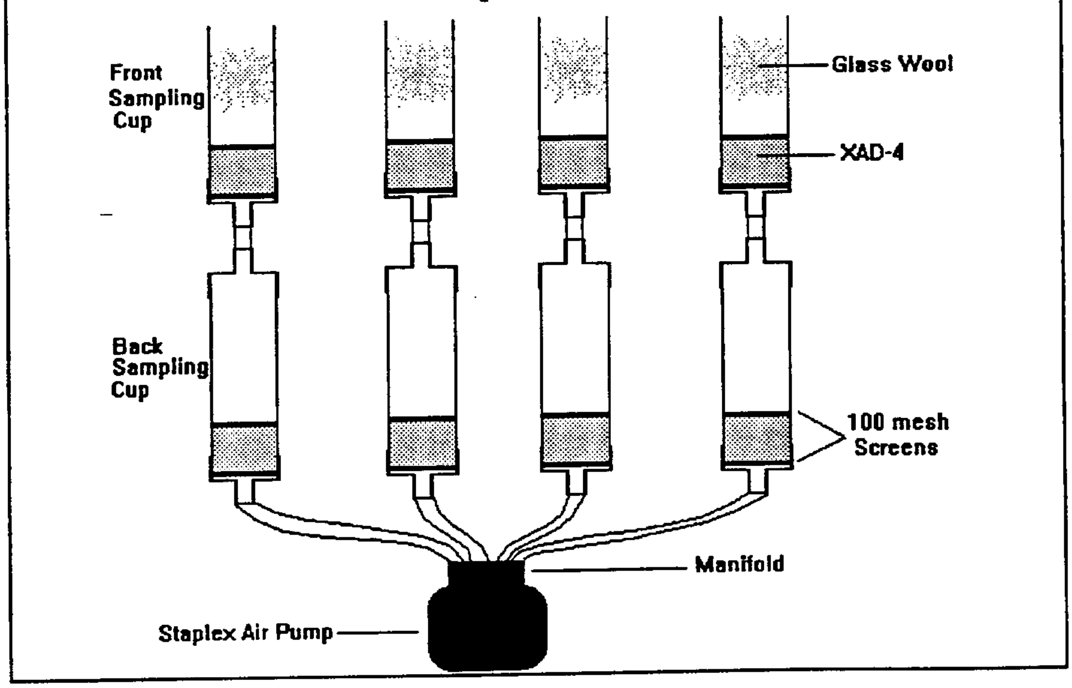


Table I, Captan Trapping Efficiency Study, 100 μg spike

Sample	Glass Wool	Front Resin	Back Resin	Total
	% Recovery			
Rep 1	99.6	14.9	<1	114.5%
Rep 2	97.1	7.6	<1	104.7%
Rep 3	120.7	5.1	<1	125.7%
Average =	105.8	9.2	<1	115.0%
SEM* =	9.2	3.6		7.5%
Control	<1	<1	<1	<3

Captan % trapping efficiency = [9.2 x 100]/[115.0-106] = 102%

Table II, THPI Trapping Efficiency Study, 100 μg Spike

Sample	Glass Wool	Front Resin	Back Resin	Total
	% Recovery			
Rep 1	21.2	42.7	<1	63.9%
Rep 2	22.5	39.6	<1	62.1%
Rep 3	13.4	43.6	<1	56.9%
Average =	19.0	41.9	<1	60.9%
SEM* =	3.5	1.5		2.6%
Control	<1	<1	<1	<3

THPI % trapping efficiency = [41.9 x 100]/[100-19] = 51.7%

*Note: SEM = Standard Error of the Mean = square root(variance/(n-1))

(4) Method Validation

Thirteen 125 ml erlenmeyer flasks were prepared by adding 30 ml of XAD-4 resin to each flask. One hundred microliters of captan (1.00 mg/ml in ethyl acetate) was added to each of the resins in a pair of flasks using a 100 μl Hamilton syringe. Similarly, 100 μl of 0.1 mg/ml was added to a second pair, and 100 μl of 0.01 mg/ml was added to a third pair. In the same manner, 100 μl of THPI (1.00 mg/ml in ethyl acetate) was added to the resin in a fourth pair. One hundred microliters of 0.1 mg/ml was added to a fifth pair, and 100 μl of 0.01 mg/ml was added to a sixth pair. The thirteenth flask was used as a control. The solvent was allowed to evaporate, and 80 ml of ethyl acetate was added to each flask. All flasks were sealed and then placed on a rotating platform for a minimum of 30 minutes. The extracts were either analyzed directly or 40 ml evaporated to the appropriate volume and then analyzed by gas chromatography. The captan and THPI results shown in Tables III and IV had good extraction recoveries (>95%) from the resin.

Table III, Captan Method Validation Study*

Amount Spiked (μg)	Replicate 1	Replicate 2	Ave % Recovery	SEM
100	91.7	100.0	95.9	5.8
10	91.3	95.8	93.6	3.2
1	112.0	120.0	116.0	6.7
			101.8	5.2

*Note: <1% of captan and THPI found in control samples at all spiked levels.

Table IV, THPI Method Validation Study*

Amount Spiked (μg)	Replicate 1	Replicate 2	Ave % Recovery	SEM
100	102.7	99.6	101.2	2.2
10	117.0	113.0	115.0	2.8
1	119.0	115.0	117.0	2.8
			111.1	3.6

*Note: <1% of captan and THPI found in control samples at all spiked levels.

(5) Freezer Stability Studies

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 captan (1.00 mg/ml in ethyl acetate) were added to the resin in jars 1, 2 and 3 using a 100 μl Hamilton syringe. Similarly, 100 μl each of 0.1 mg/ml captan were added to 4, 5, 6, and 100 μl each of 0.01 mg/ml captan were added to 7, 8 and 9. In the same manner, 100 μl of THPI (1.00 mg/ml) were added to the resin in jars 10, 11 and 12. One hundred microliters of 0.1 mg/ml THPI were added to 13, 14, 15, and 100 μl of 0.01 mg/ml THPI were added to 16, 17 and 18. Jar 19 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. Sample jars were removed and allowed to come to room temperature. Eighty mililiters of ethyl acetate were 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 captan and THPI results in Tables V and VI reflect no degradation and complete extraction of the two compounds from the resin (>95%), over the twelve-day interval.

Table V, Captan Freezer Recovery Study*

Amount Spiked (µg)	Replicate 1	2	3	Ave % Recovery	SEM
100	81.3	82.1	83.3	82.3	0.7
10	103.8	101.0	101.0	102.0	1.2
1	113.3	115.8	104.3	111.1	4.3
				98.4	4.7

Table VI, THPI Freezer Recovery Study*

Amount Spiked (µg)	Replicate 1	2	3	Ave % Recovery	SEM
100	104.6	103.5	98.6	102.3	2.3
10	111.4	116.0	108.5	112.0	2.7
1	122.8	115.9	125.4	121.4	3.5
				111.8	3.2

*Note: <1% of captan and THPI found in control samples at all spiked levels.

(6) XAD-4 Resin Preparation

1. A 61 x 29 cm cylindrical Pyrex container (approx. 40l) was thoroughly cleaned with soap and water.
2. Sixteen liters of XAD-4 resin (see note) was added to the container.
3. One gallon of methanol (Resi-grade or equivalent) was added. The resin will expand in the presence of organic solvent. This prevented rapid expansion of the resin.
4. The container was filled with deionized (DI) water with the hose placed at the bottom of the container and stirred vigorously.
5. A vacuum apparatus was prepared with a stiff tube covered at

the inlet end with gauze and the outlet end connected to a large trap.

6. As the resin settles, the "fines" were vacuumed-up. When the gauze became covered with "fines", they were wiped off and discarded.
7. The container was refilled with DI water and stirred.
8. Steps number six and seven were repeated until the water above the resin was clear.
9. The pH of the water was checked (usually about 10 from the bicarbonate coating of the resin).
10. Two liters of 0.25 N hydrochloric acid were added and stirred for 30 minutes.
11. The pH of the water was checked and then as much water as possible was removed with vacuum.
12. If the pH was >five (the pH of our DI water), then new water was added and steps nine to 11 repeated (usually at least 10 times).
13. Add one gallon of methanol and let stand overnight.
14. Pour slurry back into empty solvent bottles.
15. Eight pairs of "knee high" nylons were extracted in the thimble of a Soxlet extractor using ethyl acetate as the extraction solvent. This removed the dye from the nylons.
16. One nylon was placed inside the second to form a double wall and both were stretched directly over a Soxlet extractor chamber.
17. The slurry of methanol/resin was poured (approx. 2 l) was full of resin to just below the side arm, and the nylon tied off.
18. The resin was extracted twice for 24 hours (each time replacing the solvent) with methanol and ethyl acetate (Resi-grade) for a total of four days.
19. The cylinder of nylon/resin was removed and the resin poured into a 21 cm x 21 cm rectangular pyrex dish.
20. The resin was dried in a vacuum oven (25") for 3-4 days at 65°C.
21. The resin was transferred to a clean glass bottle for storage.

Note: XAD-4 resin, Rohm-Hass & distributed by Supelco.

(7) Gas Chromatography

Analysis of captan: concurrent, cleanup, submitted air and quality assurance samples was accomplished with a Varian Model 6000 gas chromatograph equipped with a Hall Electrolytic Conductivity Detector operated in the halogen mode and a Varian Vista Model 402 data system. The column was a "Megabore" 30 m x 0.53 mm ID DB-1. Flows for helium carrier and hydrogen were 30 and 40 ml/minute, respectively. Oven temperature program was 170°C initial with no hold time, and programmed to 230°C at 10°C/minute with a final hold time of one minute. The injector, detector base and pyrolysis furnace temperatures were 250°C, 280°C and 850°C, respectively. The total run time was seven minutes. The retention time of captan was 4.85 minutes.

Analysis of tetrahydrophthalimide (THPI): concurrent, cleanup, submitted air and quality assurance samples was accomplished with a Varian Model 3500 capillary gas chromatograph equipped with a thermionic specific detector (N/P), and a H/P Model 3396A integrator. The column was a "Megabore" a 30 m x 0.526 mm ID DB-608. Flows for helium carrier, split, makeup, hydrogen and air were 10, 30, 20, 4.5 and 175 ml/minute, respectively. Column was run "splitless" for 0.6 minute and then "split". The oven temperature program was 170°C initially with a 5.5 minute hold time, and programmed to 250°C at 30°C/minute with no final hold time. The injector and detector temperatures were 250°C and 280°C, respectively. The total run time was 8.2 minutes. The retention time of THPI was 4.75 minutes.

Analysis of captan and THPI stock solutions (see Section 8) was accomplished with a H/P Model 5890 Capillary GC equipped with a H/P model 5965A infrared detector. The column was a HP-5, 5% crosslinked phenylmethylsilicone, 25 m x 0.32 mm ID. The helium carrier flow was 1.5 ml/minute, splitless. The oven temperature was 120°C initially with a 2 minute hold time, and programmed to 250°C at 10°C/minute. The injector temperature was 250°C. The detector was liquid nitrogen cooled. THPI had a retention time of 8.60 to 8.64 minutes. The total run time was 25 minutes. Captan had a retention time of 15.72 to 15.75 minutes.

(8) Method Validation

A stock solution of captan analytical standard (Chem Service, Inc. Catalog #PS-25, purity 99.0%) was prepared. One hundred mg of standard was weighed, diluted to 100 ml in a volumetric flask with ethyl acetate (1.00 mg/ml), stoppered and mixed. A stock solution of THPI analytical standard (Chem Service, Inc. Catalog # 3305E, purity 99.0%) was made in the same manner.

Individual spiking solutions of 0.0100 mg/ml of captan and THPI were prepared by adding 1.00 ml of the 1.00 mg/ml stock solutions to a 100 ml volumetric flask with a 1.00 ml pipette. The volumetric flask was then brought up to volume with ethyl acetate, stoppered and mixed.

Concurrent recovery samples were prepared in groups of four samples. Three samples (30 ml of XAD-4 resin in a screw-top glass jar) were each fortified by adding 1.00 μg of captan spiking solution (100 μl of 0.0100 mg/ml in ethyl acetate) and 1.00 μg THPI spiking solution (100 μl of 0.0100 mg/ml in ethyl acetate) slowly on top of the resin using a 100 μl Hamilton syringe. The solvent was allowed to evaporate and the samples were capped. A fourth resin sample was used as a control. The samples were processed along with submitted samples to evaluate sample integrity during processing and analysis. Results in tables VII and VIII show good recoveries (>90%) of captan and THPI.

Table VII, Captan Concurrent Recoveries

Sample	μg Captan Added	1st %Rec	2nd %Rec	3rd %Rec	4th %Rec	5th %Rec
Control	none	<LOQ[1]	<LOQ[1]	<LOQ[1]	<LOQ[1]	<LOQ[1]
AR rep I	1.00	113	97	108	98	82
AR rep II	1.00	104	104	107	111	88
AR rep III	1.00	110	110	109	114	91
Average % Recovery =		109	103	108	108	87
Overall average % Rec =		103 ± 2.6 SEM				

[1] Note: <0.25 μg captan total (LOQ). The Limit of Quantitation (LOQ) was defined as being five times the baseline noise.

Table VIII, THPI Concurrent Recoveries

Sample	µg THPI Added	%Rec	%Rec	%Rec	%Rec	%Rec
Control	none	<LOQ[2]	<LOQ[2]	<LOQ[2]	<LOQ[2]	<LOQ[2]
AR rep I	1.00	103	97	97	85	86
AR rep II	1.00	111	102	101	97	95
AR rep III	1.00	114	103	106	97	92
Average % Recovery =		109	101	101	93	91
Overall average % Rec =		99	± 2.1 SEM			

[2] Note: <0.5 µg THPI Total (LOQ). The Limit of Quantitation (LOQ) was defined as being five times the baseline noise.

(9) Sample Preparation

Samples that had been refrigerated were allowed to come to room temperature on the benchtop before sample processing. Eighty ml of ethyl acetate was added to each sample. Samples were capped and placed on a rotating platform for a minimum of thirty minutes. Forty ml (1/2 sample) was measured using a graduated cylinder and placed into a 100 ml round bottom flask. The solvent was evaporated on a rotary evaporator (30°C) until dry, two ml of ethyl acetate (or as appropriate) was added, and the sample mixed and stoppered until analysis.

A limit of quantitation (LOQ) for captan and THPI was established at <0.25 and <0.5 total µg per sample, respectively. The Limit of Quantitation (LOQ) was defined as being five times the baseline noise and calculated based on three microliter injections, and a peak height of less than <15 mm or <10 mm for captan and THPI, respectively. This yielded a concentration of <0.18 ng Captan/3 µl and <0.33 ng THPI/3 µl. The calculation would be:

<0.25 µg captan = (<0.18 ng/3 µl injected) x (2 ml final volume) x (80 ml original volume/40 ml taken)

<0.5 µg THPI = (<0.36 ng/3 µl injected) x (2 ml final volume) x (80 ml original volume/40 ml taken)

(10) Sample Cleanup

A florisil cleanup was developed to remove interferences from the samples in the analysis of THPI. Any samples that had THPI residues were processed through this cleanup and reanalyzed. This cleanup also separated the parent compound, captan, from the metabolite, THPI. The florisil cleanup column was prepared as follows: a 10 mm ID x 10 cm glass column with a 125 ml reservoir was packed with 1 cm of glass wool, followed by 1 cm of anhydrous sodium sulfate and 5 cm of 60/80 mesh florisil used directly from a 105°C oven. The freshly prepared column was prewashed with 15 ml of hexane, and the sample from the round bottom flask was added to the column in 5 ml of hexane, just as the prewash was sinking into the column surface. The original round bottom flask was washed twice with 5 ml of hexane and added to the column as before. The column was eluted with 25 ml of hexane and the eluate discarded. The column was then eluted with 50 ml of 10% ethyl ether in hexane and discarded. The column was then eluted with 35 ml of 20% ethyl acetate in hexane and the eluate collected as "Cut I" into a 100 ml round bottom flask. This fraction contains the parent compound, captan. The column was finally eluted with 60 ml of ethyl acetate as "Cut II" into a 250 mL round bottom flask. This fraction contains the captan metabolite, THPI. "Cut I" and "Cut II" were evaporated on a rotary evaporator (30°C) and the samples redissolved in 2 ml of ethyl acetate (or as appropriate) for analysis.

To validate the cleanup, seven previously analyzed ARB samples which had negligible residues were used. Samples 2, 4 and 5 were each fortified by adding 1.00 µg of captan spiking solution (100 µl of 0.0100 mg/ml in ethyl acetate) and 1.00 µg THPI spiking solution (100 µl of 0.0100 mg/ml in ethyl acetate) slowly on top of the resin using a 100 µl Hamilton syringe. The solvent was allowed to evaporate and the samples were capped. Samples 6, 7 and 10 were each fortified by adding 10.0 µg of captan stock solution (10.0 µl of 1.00 mg/ml in ethyl acetate) and 10.0 µg THPI stock solution (10.0 µl of 1.00 mg/ml in ethyl acetate) slowly on top of the resin using a 10 µl Hamilton syringe. The solvent was allowed to evaporate and the samples were capped. Sample 1 was used as a control.

The prepared samples were processed through the previously described cleanup method and yielded good recoveries (90% or above) for both captan and THPI (see Table IX).

Table IX, Cleanup Validation Samples

Sample	μg captan Spiked	captan % Rec	Ave % Rec	μg THPI Spiked	THPI % Rec	Ave % Rec
1	none	<LOQ	<LOQ	none	<LOQ	<LOQ
2	1.00	99		1.00	94	
4	1.00	98		1.00	87	
5	1.00	97	98	1.00	90	90
6	10.0	99		10.0	90	
7	10.0	100		10.0	90	
10	10.0	94	98	10.0	89	90
Overall Average % Recovery =			98			90

(11) Working Standard Preparation

Working standards of captan were prepared by adding 25 μl of 1.00 mg/ml captan stock solution (see Section 8) to volumetric flasks of increasing size: 25 ml, 50 ml, 100 ml, and 200 ml. The flasks were diluted to volume with ethyl acetate, stoppered and mixed. This yielded captan concentrations of 1.00, 0.500, 0.250, and 0.125 ng/μl captan, respectively. A fifth captan working standard of 0.0625 ng/μl was made. One hundred ml of the 0.125 ng/μl standard was added to a 200 ml volumetric, diluted to volume, stopped and mixed.

Working standards of THPI were prepared by adding 25 μl of 1.00 mg/ml THPI stock solution (see Section 8) to volumetric flasks of increasing size: 50 ml, 100 ml, 200 ml. The flasks were diluted to volume with ethyl acetate, stoppered and mixed. This yielded

THPI concentrations of 0.500, 0.250 and 0.125 ng/µl THPI, respectively.

(12) Submitted Air Samples

On 5/14/93, sixteen ambient air samples were transferred by Jack Rogers, to the Trace Analytical Laboratory (TAL) for analysis. The samples were in an ice chest with dry ice. The samples were in a frozen condition and labeled 1A-1 through 3BL. The samples were inspected, assigned unique TAL log numbers and placed into a -20°C freezer until extracted. On 5/21/93 (7 days from receipt), the samples were extracted (see Section 9), the samples were cleaned-up, if necessary (see Section 10), and compared to working standards (See section 11). The results of analysis are shown in Table X.

On 5/21/93, twenty-one ambient air samples were delivered by courier to TAL for analysis. The samples were in an ice chest with dry ice. The samples were in a frozen condition and labeled 4E through 7BL. The samples were inspected, assigned unique TAL log numbers, and extracted the same day. It was noted that the samples appear to have only 15 to 20 ml of resin in a jar (visual evaluation against another jar with a known volume) instead of the 30 ml volume stated in the protocol. The results of analysis are shown in Table X. Four concurrent recovery samples, a control and three samples of 1.0 µg each captan and THPI, were also extracted (see Section 8) on the same day along with the submitted samples. The results for the concurrent recovery samples are shown in the "1st" column in Tables VII and VIII. Recoveries were excellent for both captan (109%) and THPI (109%).

On 5/28/93, sixty-two samples total were delivered to TAL in three boxes by Don Fitzell for analysis. The samples were in an ice chest with dry ice. There were forty-one application samples and twenty-one ambient samples. Box I contained twenty-one ambient air samples labeled 8E-1 through 11BL and one unused jar. Box II contained twenty-four application air samples labeled OS-1 through 4E. Box III contained seventeen application air samples labeled 4N through 7W. The samples were inspected, assigned unique TAL log numbers and placed into a -20°C freezer until extracted. On 6/4/93, the samples were extracted (6 days from receipt)(see Section 9), cleaned-up, if necessary (see Section 10), and compared to working standards (see Section 11). The results for the ambient samples are shown in Table X, and the application samples in Table XI. Four concurrent recovery samples, a control and three samples of 1.0 μg each captan and THPI, were also processed (see Section 8) on the same day along with the submitted samples. The results for the concurrent recovery samples are shown in "2nd through 5th" columns in Tables VII and VIII. Note that this represents daily re-analysis of the same set of concurrent samples (extracted on 6/4/93). Recoveries were acceptable for both captan (87 to 108%) and THPI (91 to 101%).

On 6/4/93, Ken Lewis delivered sixteen ambient air samples in an ice chest with dry ice. The samples were in a frozen condition, and labeled 12A through 14BF. The samples were inspected and assigned unique TAL log numbers. The samples were extracted (see Section 9) on the same day, cleaned up if necessary (see Section 10), and compared to working standards (see Section 11). The results are shown in Table X. Note that the concurrent recovery samples for the samples submitted on 5/28/93 also apply to these samples, since they were all extracted on the same day.

Table X- Submitted Ambient Samples

ARB Log #	ARB ID	Collected	Type	Total μg Captan	Total μg THPI
1	1A-1	5/11/93	resin	<0.25	<0.5
2	1A-2	"	"	<0.25	<0.5
3	1M	"	"	<0.25	<0.5
4	1E	"	"	<0.25	<0.5
5	1B	"	"	<0.25	<0.5
6	2A-1	5/12/93	resin	<0.25	<0.5
7	2A-2	"	"	<0.25	<0.5
8	2M	"	"	<0.25	<0.5
9	2E	"	"	<0.25	<0.5
10	2B	"	"	<0.25	<0.5
11	3A-1	5/13/93	resin	<0.25	<0.5
12	3A-2	"	"	<0.25	<0.5
13	3M	"	"	<0.25	<0.5
14	3E	"	"	<0.25	<0.5
15	3B	"	"	<0.25	<0.5
16	3BL	"	blank	<0.25	<0.5
17	4E	5/18/93	resin	<0.25	<0.5
18	4A	"	"	<0.25	<0.5
19	4M-1	"	"	<0.25	<0.5
20	4M-2	"	"	<0.25	<0.5
21	4BF	"	"	<0.25	<0.5
22	5E	5/19/93	resin	<0.25	<0.5
23	5A	"	"	<0.25	<0.5
24	5M-1	"	"	<0.25	<0.5
25	5M-2	"	"	<0.25	<0.5
26	5BF	"	"	<0.25	<0.5
27	6E	5/20/93	resin	<0.25	<0.5
28	6A	"	"	<0.25	<0.5
29	6M-1	"	"	<0.25	<0.5
30	6M-2	"	"	<0.25	<0.5
31	6BF	"	"	<0.25	<0.5
32	7E	5/21/93	resin	<0.25	<0.5
33	7A	"	"	<0.25	<0.5
34	7M-1	"	"	<0.25	<0.5
35	7M-2	"	"	<0.25	<0.5
36	7BF	"	"	<0.25	<0.5
37	7BL	"	blank	<0.25	<0.5

Table X- Submitted Ambient Samples: continued

ARB Log #	ARB ID	Collected	Type	Total µg Captan	Total µg THPI
38	8E-1	5/25/93	resin	<0.25	<0.5
39	8E-2	"	"	<0.25	<0.5
40	8A	"	"	<0.25	<0.5
41	8M	"	"	<0.25	<0.5
42	8BF	"	"	<0.25	<0.5
43	9E-1	5/26/93	resin	<0.25	<0.5
44	9E-2	"	"	<0.25	<0.5
45	9A	"	"	<0.25	<0.5
46	9M	"	"	<0.25	<0.5
47	9BF	"	"	<0.25	<0.5
48	10E-1	5/27/93	resin	<0.25	<0.5
49	10E-2	"	"	<0.25	<0.5
50	10A	"	"	<0.25	<0.5
51	10M	"	"	<0.25	<0.5
52	10BF	"	"	<0.25	<0.5
53	11E-1	5/28/93	resin	<0.25	<0.5
54	11E-2	"	"	<0.25	<0.5
55	11A	"	"	<0.25	<0.5
56	11M	"	"	<0.25	<0.5
57	11BF	"	"	<0.25	<0.5
58	11BL	"	Blank	<0.25	<0.5
59	12A	6/2/93	resin	<0.25	<0.5
60	12M	"	"	<0.25	<0.5
61	12E-1	"	"	<0.25	<0.5
62	12E-2	"	"	<0.25	<0.5
63	12BF	"	"	<0.25	<0.5
64	13A	6/3/93	resin	<0.25	<0.5
65	13M	"	"	<0.25	<0.5
66	13E-1	"	"	<0.25	<0.5
67	13E-2	"	"	<0.25	<0.5
68	13BF	"	"	<0.25	<0.5
69	13BL	"	blank	<0.25	<0.5
70	14A	6/4/93	resin	<0.25	<0.5
71	14M	"	"	<0.25	<0.5
72	14E-1	"	"	<0.25	<0.5
73	14E-2	"	"	<0.25	<0.5
74	14BF	"	"	<0.25	<0.5

Table XI- Submitted Application Samples

ARB Log #	ARB ID	Collected	Type	Total μg Captan	Total μg THPI
1	0S-1	5/24/93	resin	<0.25	<0.5
2	0S-2	"	"	<0.25	<0.5
3	0E	"	"	<0.25	<0.5
4	0N	"	"	<0.25	<0.5
5	0W	"	"	<0.25	<0.5
6	1S-1	5/25/93	resin	0.30	<0.5
7	1S-2	"	"	<0.25	<0.5
8	1E	"	"	0.41	<0.5
9	1N	"	"	<0.25	<0.5
10	1W	"	"	0.94	<0.5
11	2S-1	5/25/93	resin	<0.25	<0.5
12	2S-2	"	"	<0.25	<0.5
13	2E	"	"	<0.25	<0.5
14	2N	"	"	<0.25	<0.5
15	2W	"	"	<0.25	<0.5
16	2B	"	"	<0.25	<0.5
17	3S-1	5/25/93	resin	<0.25	<0.5
18	3S-2	"	"	<0.25	<0.5
19	3E	"	"	<0.25	<0.5
20	3N	"	"	<0.25	<0.5
21	3W	"	"	<0.25	<0.5
22	4S-1	5/25/93	resin	<0.25	<0.5
23	4S-2	"	"	<0.25	<0.5
24	4E	"	"	<0.25	<0.5
25	4N	"	"	<0.25	<0.5
26	4W	"	"	<0.25*	<0.5
27	5S-1	5/26/93	resin	<0.25	<0.5
28	5S-2	"	"	<0.25	<0.5
29	5E	"	"	<0.25	<0.5
30	5N	"	"	<0.25	<0.5
31	5W	"	"	0.25	<0.5
32	6S-1	5/27/93	resin	<0.25	<0.5
33	6S-2	"	"	<0.25	<0.5
34	6E	"	"	<0.25	<0.5
35	6N	"	"	<0.25	<0.5
36	6W	"	"	<0.25	<0.5
37	7S-1	5/28/93	resin	<0.25	<0.5
38	7S-2	"	"	<0.25	<0.5
39	7E	"	"	<0.25	<0.5
40	7N	"	"	<0.25	<0.5
41	7W	"	"	<0.25	<0.5

*Note: Trace amount detected

(13) Submitted Quality Assurance Samples

On 6/1/93, a courier delivered to TAL one can containing standards of captan and THPI and one box of resin samples from G. Ruiz. The standards were used for characterization (see Section 14). The box contained "blue ice" and seven resin samples labeled CPN-1 through CPN-7. The samples were in a frozen condition. The resin samples were inspected, assigned unique TAL log numbers and extracted the same day. The samples were processed (see Section 9), and compared to working standards (see Section 11). The results are shown in Table XII.

Table XII, Submitted Quality Assurance Samples

ARB Log #	ARB ID	μg Captan	μg THPI
n/a	CPN-1	5.38	3.40
n/a	CPN-2	3.26	5.13
n/a	CPN-3	<0.25	<0.50
n/a	CPN-4	10.29	0.59
n/a	CPN-5	3.35	5.55
n/a	CPN-6	<0.25	9.75
n/a	CPN-7	5.57	3.33

(14) Standards Characterization

On 6/1/93, samples of captan (0.206 mg/ml in ethyl acetate) and THPI (0.2 mg/ml in ethyl acetate) were submitted along with seven quality assurance samples by G. Ruiz. The FT-IR characterization of the captan and THPI solutions were made by directly injecting 1 μl of each on the FT-IR (see Section 7). The identity of captan and THPI was confirmed by comparison to known IR spectra. The submitted THPI solution was then diluted to 1.00 ng/μl by adding 250 μl to a 50 ml volumetric with ethyl acetate. Three μl was injected directly on the Varian gas chromatograph used for THPI analysis (see Section 7), and then compared to the diluted analytical standard (see Section 11) yielding a purity of 97%.

The submitted captan solution was diluted to 0.250 ng/μl with ethyl acetate by adding 121.3 μl to a 100 ml volumetric flask. The resulting solution was injected directly on the Varian gas chromatograph used for captan analysis (see Section 7) and then compared to the diluted analytical standard (see Section 11) yielding a purity of 103%. To determine the THPI content of the submitted captan standard, 485.4 μl (100 μg) of the standard was evaporated in a 50 ml round bottom flask, 5 ml of hexane added, mixed and cleaned up through a florisil cleanup (see Section 10). The THPI fraction was evaporated on a rotary evaporator and re-dissolved in 2 ml of ethyl acetate. The THPI fraction was then injected on the Varian gas chromatograph used for THPI analysis (see Section 7), and then compared to the diluted THPI analytical standard (see Section 11), yielding a THPI concentration of 0.93% in the submitted captan standard.

Appendix I: Carbofuran Application Monitoring Report (ARB/EEB)

State of California

AIR RESOURCES BOARD

AMBIENT AIR MONITORING FOR CARBOFURAN IN IMPERIAL COUNTY DURING SPRING 1993, AFTER AN APPLICATION TO AN ALFALFA FIELD

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C93-013A

Report Date: March 24, 1994

APPROVED:

D. Fitzell, Project Engineer
Testing Section

Peter K. Ouchida Manager
Testing Section

George Lew, Chief
Engineering Evaluation Branch

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

Ambient Air Monitoring for Carbofuran in Imperial County during Spring 1993, after an Application to an Alfalfa Field

This report presents the results of ambient air monitoring for carbofuran after a ground application at a selected alfalfa field in Imperial County. Detected concentrations varied from 0.03 to 0.66 ug/m^3. The results are based on samples collected by the Air Resources Board Engineering Evaluation Branch staff and analyzed by the Trace Analytical Laboratory, Department of Environmental Toxicology at U.C. Davis. The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

Jack Rogers was the Instrument Technician. Linda Evans of the Imperial County Office of the Agricultural Commissioner assisted in arranging for a suitable field to monitor. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses were performed by the Trace Analytical Laboratory, Department of Environmental Toxicology of the University of California, Davis.

State of California
Air Resources Board

Ambient Air Monitoring for Carbofuran in Imperial County during Spring 1993, after an Application to an Alfalfa Field

I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a two-day source impacted ambient monitoring program for carbofuran in Imperial County during the Spring of 1993. As required by AB 1807, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

The Pesticide Use Report for 1991 indicated the predominant use for carbofuran was alfalfa, followed by grapes, rice and sugarbeets. The peak use for alfalfa was February - March in Imperial County.

II. DESCRIPTION

Carbofuran (molecular weight 221.26 g/mole) is a broad spectrum insecticide used on various crops for a variety of pests. Chemically it is a white, odorless solid with a melting point of 153-154°C. It has a vapor pressure of 3.1×10^{-7} mbar at 20°C. It is nearly insoluble in water and n-hexane, but is soluble in 2-propanol and readily soluble in dichloromethane. The oral LD_{50} for rats is 11 mg/kg and the dermal LD_{50} for rabbits is 10,200 mg/kg (1990 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

An alfalfa field of about 70 acres was selected (FIGURE I) by Linda Evans of the Imperial County Office of the Agricultural Commissioner and approved by ARB staff to use for application monitoring. Five samplers were set up: (1) two (collocated) approximately 20 yards north of the field, (2) one approximately 20 yards south of the field (3) one approximately 20 yards east of the field and (4) one approximately 20 yards west of the field. A meteorological station was set up near the southern sampler (FIGURE II). The application occurred on March 31, 1993 and the monitoring continued until the morning of April 2.

The insecticide was applied from west to east using a pickup truck pulling a tank with booms. The application took one hour to complete at the rate of one and one-quarter pints Furadan (containing 44% active ingredient, carbofuran) per acre. The Notice of Intent is included as APPENDIX I.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through XAD-4 resin (see APPENDIX II). The holders were made of Teflon and contained approximately 30 cc of resin. 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 transported on dry ice to the Trace Analytical Laboratory (TAL) of the Department of Environmental Toxicology (DET), University of California, Davis for analysis.

Sampling trains designed to operate continuously were set up at the sampling sites identified in FIGURE II. Duplicate samples were obtained from the site designated "N". Resin was changed, as closely as practical, according to the schedule outlined in the QA Plan for Pesticide Monitoring (APPENDIX III).

Each sample train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, train support, and a 12VDC battery-powered vacuum pump. A diagram of the sampling train is shown in FIGURE III. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through the resin holder adjusted with a metering valve to an indicated reading of 12.4 on a flow meter. This was accomplished by attaching a calibrated flow meter to the inlet of the resin holder. 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 12.4 and was recorded (if different from the planned lpm) along with date, time and site location. Calibration prior to use in the field indicated that an average flow rate of 16.2 lpm was actually achieved when the flow meter was set to 12.4.

At the end of each sampling period the final indicated flow rate (if different than the set 12.4), the stop date and time were recorded. The XAD-4 resin was then removed from the holder, transferred to a precleaned jar with a Teflon-lined lid and an identification label affixed to each jar. Each jar was then placed in an ice chest containing dry ice until the jars were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the TAL staff. The XAD-4 was extracted with 75 ml of ethyl acetate, concentrated, followed by GC separation on a DB-5 megabore column and measurement by a Thermionic Specific (nitrogen/phosphorous) Detector (TSD) (APPENDIX IV). The minimum detection limit was 5 times the baseline noise.

VI. RESULTS

Results for carbofuran are shown in TABLE I and APPENDIX IV. Many of the flow rates decreased from the original set value for the samples in the 5 and 6 series (e.g., 5W, 6N-1, etc.). The reported values (TABLE I) were calculated using the average of the beginning and ending flow rates. The final concentrations were also calculated using the beginning flow rate and the final flow rate separately. This would give minimum and maximum concentrations possible. It was found the resultant concentrations varied from the reported values by no more than plus or minus the least significant digit reported. TABLE II is a summary of the meteorological data collected on site. TABLE III is a pictographic summary of both the meteorological and sampling data. As TABLE I shows, low levels of carbofuran were found. The values were fairly evenly distributed between the lowest and highest measured concentrations, 0.03 to 0.66 ug/m^3.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Laboratory Reports for Carbofuran (APPENDIX IV).

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX III) were followed. The Quality Management and Operations Support Branch (QMOSB) of the ARB conducted a flow audit of the samplers as well as a laboratory audit of the DET at U.C. Davis. This report is included as APPENDIX V. As shown in APPENDIX V, the flow rates were within 2% of the reported rate and the recovery of the spiked samples by DET were from 10% below the spiked level to 5% above the spiked level.

Table I. Carbofuran Monitoring Data

Sample ID	Time (min.)	Volume (m^3)	Amount Detected* (ug)	Concentration (ug/m^3)	Collection Time (Approx.)
0W	85	1.37	ND	--	(Background) 3/31/93 0800-0930
0N-1	95	1.53	ND	--	
0N-2	95	1.53	ND	--	
0E	95	1.53	ND	--	
0S	85	1.37	ND	--	
1W	65	1.05	0.3	0.29	(Application) 3/31/93 1000-1100
1N-1	90	1.45	ND	--	
1N-2	90	1.45	ND	--	
1E	85	1.37	0.9	0.66	
1S	90	1.45	ND	--	
2W	165	2.66	1.3	0.49	3/31/93 1100-1400
2N-1	165	2.66	0.9	0.34	
2N-2	165	2.66	0.6	0.23	
2E	170	2.74	0.4	0.15	
2S	165	2.66	ND	--	
2B	BLANK	--	ND	--	
3W	210	3.38	1.8	0.53	3/31/93 1400-1730
3N-1	215	3.46	1.9	0.55	
3N-2	215	3.46	2.3	0.66	
3E	210	3.38	0.9	0.27	
3S	215	3.46	ND	--	
4W	215	3.46	0.9	0.26	3/31/93 1730-2100
4N-1	210	3.38	0.7	0.21	
4N-2	210	3.38	0.7	0.21	
4E	210	3.38	0.5	0.15	
4S	210	3.38	ND	--	
5W	605	9.62	0.3	0.03	3/31-4/1/93 2100-0700
5N-1	605	9.44	0.7	0.07	
5N-2	605	9.44	0.8	0.08	
5E	610	9.70	2.0	0.21	
5S	610	9.70	1.1	0.11	
6W	1410	22.63	0.8	0.04	4/1-2/93 0700-0600
6N-1	1400	20.38	1.3	0.06	
6N-2	1400	22.47	1.3	0.06	
6E	1395	22.18	2.6	0.12	
6S	1380	21.94	1.0	0.05	
6B	BLANK	--	ND	--	

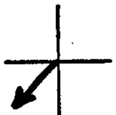
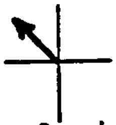
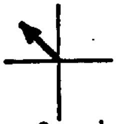
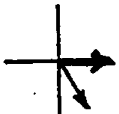
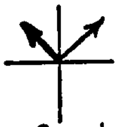
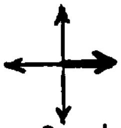
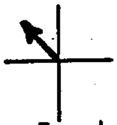
*ND = Not Detected, less than the limit of quantitation, 0.3 ug/sample.

Table II. Carbofuran Meteorological Data

Sampling Period	Date	Time	Wind Speed (mph)	Wind Direction*
0	3/31	0800-0930	1	**NE**
1	3/31	1000-1100	2	**SE**
2	3/31	1100-1400	3	**SE**/SW
3	3/31	1400-1730	5	**SE**
4	3/31	1730-2100	2	**SE**
5	3/31-4/1	2100-0700	2	**W**/NW
6	4/1-4/2	0700-0600	8	**W**/N/S/E

*indicates direction wind is blowing from. **BOLD** indicates predominant wind direction, if any.

TABLE III. Summary of Carbofuran Application Data ($\mu g/m^3$)

(0) [N] ND* [W] ND  1 mph [E] ND [S] ND	(4) [N] 0.21* [W] 0.26  2 mph [E] 0.15 [S] ND
(1) [N] ND* [W] 0.29  2 mph [E] 0.66 [S] ND	(5) [N] 0.08* [W] 0.03  2 mph [E] 0.21 [S] 0.11
(2) [N] 0.28* [W] 0.49  3 mph [E] 0.15 [S] ND	(6) [N] 0.06* [W] 0.04  8 mph [E] 0.12 [S] 0.05
(3) [N] 0.60* [W] 0.53  5 mph [E] 0.27 [S] ND	

*Average of two collocated samples.
( ) Indicates sampling period. [ ] Indicates sampling site represented.
Arrow indicates direction wind is blowing toward. Bold indicates predominant wind direction, if any.
ND = not detected, less than the limit of quantitation, 0.3 ug/sample.

Figure I. Carbofuran Monitoring Area

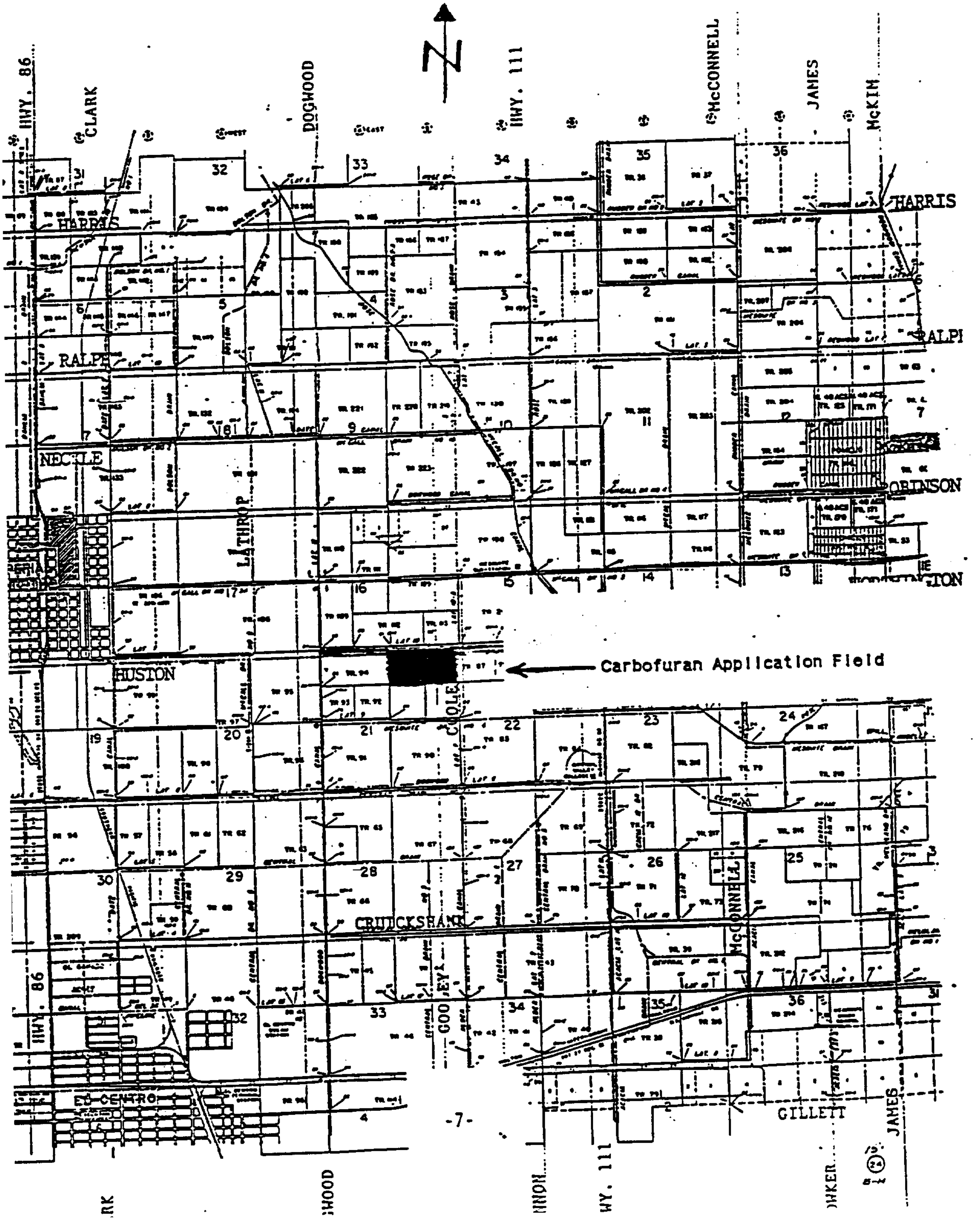


Figure II. Carbofuran Monitoring Sites

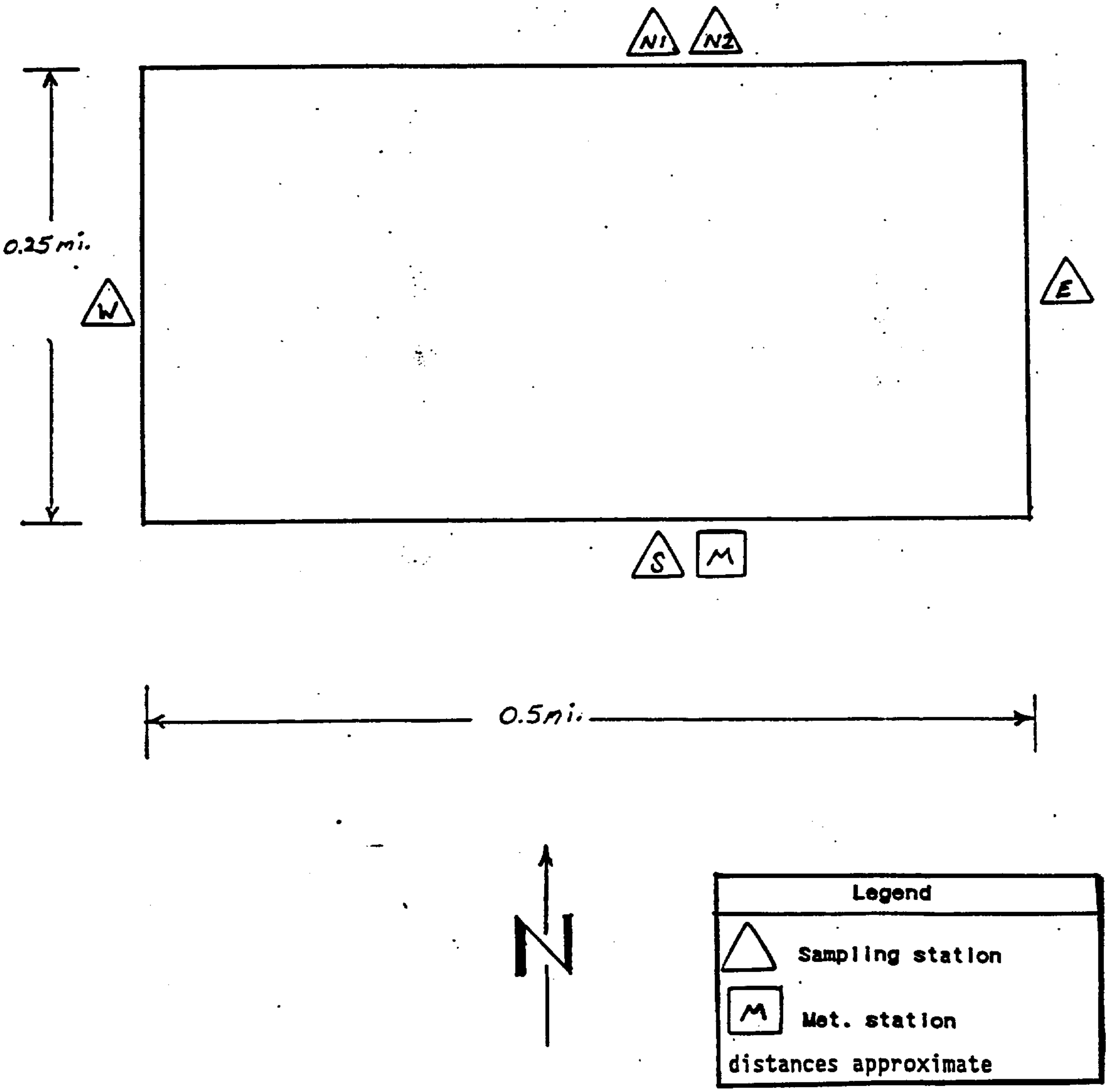
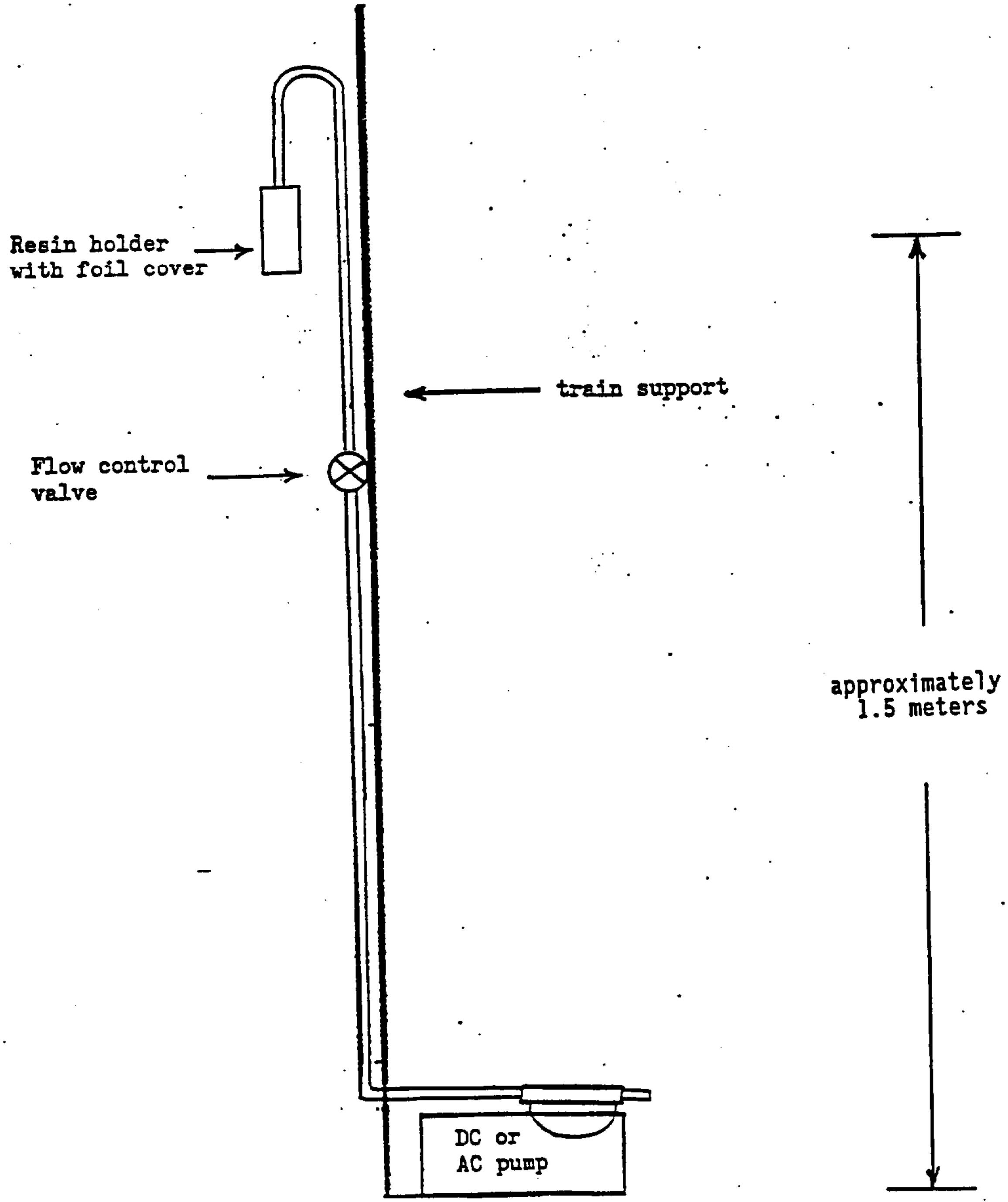


Figure III. Carbofuran Monitoring Apparatus



APPENDIX I

NOTICE OF INTENT

№ 1843 PERMIT NO. 13-93-1302654

IMPERIAL
COUNTY NO. 13

NOTICE OF INTENT TO APPLY RESTRICTED MATERIALS ☐ And/Or RECOMMENDATION ☐

COMP. DATE

LAST TREATED 15 Mar 93

HAR. DATE EST.

GROWER–PERMITTEE Alex Abatti Jr Farming

NOTIFIED

LOCATION Dogwood 74 North ✓

RANCH

SEC	TWN	RNG	MAP ID
21	15	14	7

ACRES 70

COMMODITY/SITE Alfalfa ✓

DILUTION/VOLUME GALS

RATE PER ACRE 5 [✓ GALS] L

APPLICATION DATE 30 March 93 ✓

AIR – FW – REL – G

SUPPLIER Rockwood & Helena

INVOICE #

NOTIFIED

W.O. #

PEST CONTROL OPERATOR Alex Abatti Jr Farming

ADDRESS

NOTIFIED

RATE/AC		PESTICIDE	TOTAL
1.25	[✓ PTS] QTS GALS - LBS	Furadan 4F ✓ (Rockwood)	11 GA
.5	PTS - QTS GALS - LBS	Diazinon AG500 (Helena)	5 GA
	PTS - QTS GALS - LBS	(Rockwood) 10-15-0	1 GA
	PTS - QTS GALS - LBS		GA
	PTS - QTS GALS - LBS		GA

PESTS

ALF CATERPILLAR	
ALF WEEVIL	✓
APHIDS	✓
ARMYWORM	
BEETLES	
BOLLWORM	
BUDWORM	
CHALCID FLY	
CRICKETS	
CUTWORM	
GRASSHOPPERS	
LEAF MINER	
LEAF PERFORATOR	
LEAFHOPPER	
LOOPER	
LYGUS BUG	
PINK BOLLWORM	
SALT MARSH CATERPILLER	
SPIDER MITES	
SPOTTED ALF APHID	
STINK BUG	
THRIPS	
WHITEFLY	
WEEDS	
DEFOLIATION / DES	
MILDEW	

ENVIRONMENTAL CHANGES:
No Bloom in field
No geese widgeon or
Coots are known to be
frequenting the treatment
area for feeding

Alfa	Alfa	House
Alfa	N W TREAT AREA E S	Alfa
Alfa	Sugar	Wheat

RESTRICTIONS:
48 HRS./DAYS RE-ENTRY
___ AFTER DRIFT & VAPOR GONE
___ AFTER SPRAY DRIES
14 DAYS TO HARVEST
___ DAYS TO PASTURE
___ DO NOT FEED OR GRAZE LIVESTOCK ON CROP WASTE FOR ___ DAYS
✓ AVOID DRIFT TO SURROUNDING AREAS
✓ TOXIC TO BIRDS, BEES, FISH & WILDLIFE

REMARKS — SPECIAL INSTRUCTIONS — C-WR-B-RB-NIB-CD-WIN-PAS-I-W-O-W-GRI-CR-EQ-SD-CUL-LB-N..

EVALUATION CRITERIA

☐ Sweep Counts
☐ Trap Counts
☑ % Infestation
☐ Preventative
☑ Alternate mitigation measures have been considered
☑ Economic Damage Imminent

SUBMITTED AND/OR RECOMMENDED BY

LICENSE NO. 6637

FILE DATE 29 Mar 93

TIME

DATE

APPROVED

DENIED

AGRICULTURAL COMMISSIONER

3/29/93

APPENDIX II

SAMPLING PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

Carbofuran Monitoring in Imperial County during Spring, 1993

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C93-013A

Date: May 19, 1993

APPROVED:

__________________, Project Engineer
Testing Section

Peter Ouchida, Manager
Testing Section

George Lew, Chief
Engineering Evaluation Branch

Protocol for Carbofuran Monitoring
in Imperial County during Spring, 1993

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) Engineering Evaluation Branch (EEB) will conduct a 3-day source impacted ambient monitoring program upwind and downwind of an application of carbofuran to determine concentrations near an application. Carbofuran is a broad spectrum insecticide used on a wide variety of crops for various pests. A report on the measured concentrations will be submitted to DPR.

II. Sampling

A stainless steel valve down stream of the sampling medium will be used to control all sample flow rates. The flow rate will be set and checked with a calibrated flowmeter. Carbofuran will be collected on a bed of XAD-4 resin. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. Any change in the flow rates will be recorded in a log book, along with any other pertinent information.

Prior to application, background samples will be taken to establish if any carbofuran is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with DC-powered pumps capable of flows of approximately 16 liters per minute. Sample collection will follow the timetable outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" as closely as is reasonably possible.

Five samplers will be used; each approximately 20 yards from the perimeter of the field. Four will be placed at the center of each face (assuming a rectangular field) of the field. The fifth sampler will be collocated with one of the other samplers to obtain precision data. These distances and locations are approximate and dependent on the physical obstacles surrounding the field. ARB's "Quality Assurance Plan for Pesticide Monitoring" will be followed as closely as possible.

III. Analysis

All samples will be analyzed by the Department of Environmental Toxicology (DET), University of California, Davis. The resin will first be extracted with ethyl acetate to remove carbofuran. The carbofuran will be separated on a DB-5 (or similar) column and measured with a thermionic specific detector (nitrogen/phosphorous).

IV. Quality Assurance

Field sampling and laboratory analytical quality assurance activities are described in the ARB's "Quality Assurance Plan for Pesticide Monitoring."

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. Sample flow rates will be calibrated prior to and after sampling in the field.

A chain of custody sheet will accompany all samples. A field log book will be used to record start and stop times, sample ID's and any other significant data, including field size, application rate, formulation, and length of the application.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers (Instrument Technician).

APPENDIX III

QUALITY ASSURANCE PLAN

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN
FOR PESTICIDE MONITORING

Prepared by the

Monitoring and Laboratory Division

and

Stationary Source Division

Revised: February 4, 1994

APPROVED:

Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch

Cook, Chief
Quality Management and Operations
Support Branch

George Lew, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signifiy 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.

TABLE OF CONTENTS

APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).
3. Specification of sampling periods and flow rates.
4. Description of the analytical method.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

   A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

   Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

   The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

   Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

   The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

   All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: ______________ **Date:** ____/____/____
Sample/Run #: ______________ **Time:** ______________
Job name: ______________________________
Sample Location: ______________________________
Type of Sample: ______________________________
Log #'s: __________

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: ______________________________

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX IV

LABORATORY REPORT

Refer to Chapter 2 Captan Application and Ambient Monitoring Report (TAL)

APPENDIX V

QMOSB AUDIT REPORT

June 30, 1993

AUDIT REPORT

CARBOFURAN MONITORING IN IMPERIAL COUNTY

SUMMARY

Between March 31 and April 2, 1993, the Engineering Evaluation Branch of the California Air Resources Board conducted ambient air sampling to document the airborne emissions of Carbofuran during an application in Imperial County, California. The samples were analyzed by the Trace Analytical Laboratory of the UC Davis Department of Environmental Toxicology.

On March 11, staff of the Quality Assurance Section of the Air Resources Board conducted flow rate audits of the air samplers used in the monitoring of Carbofuran. The audits were conducted with a mass flow meter traceable to the National Institute of Standards and Technology. The difference between the reported and true flow rates averaged -0.6% with a range of -1.2% to 0%.

A system audit of the Trace Analytical Laboratory was conducted to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that these were consistent with good practice. The only deficiencies noticed were the lack of control charts or response factor plots, and field spikes.

On April 15, seven samples spiked with measured amounts of Carbofuran were submitted to the laboratory for analysis. The samples were prepared from a 0.2 mg/ml Carbofuran solution obtained from Chem Service. The difference between the assigned and the reported Carbofuran mass averaged -4.0% and ranged from -10.0% to 5.0%.

AUDIT REPORT

CARBOFURAN MONITORING IN IMPERIAL COUNTY

INTRODUCTION

Between March 31 and April 2, 1993, the Engineering Evaluation Branch (EEB) of the California Air Resources Board (CARB) conducted ambient air sampling to document the airborne emissions of Carbofuran during an application in Imperial County, California. Samples were collected in the vicinity of the treated field by drawing ambient air at measured rates through sampling cups containing an adsorbant resin. The samples were later analyzed by the Trace Analytical Laboratory (TAL) of the UC Davis Department of Environmental Toxicology. Gabriel Ruiz of the CARB's Quality Assurance (QA) Section conducted a flow rate audit of the air samplers, a system audit of the field and laboratory operations, and a performance audit of the analytical method.

FLOW RATE AUDIT

On March 11, 1993, a flow rate audit of the five air samplers used by the EEB in the monitoring of Carbofuran was conducted at the EEB's shop in Sacramento, before the samplers were deployed in the field.

Each sampler consisted of a sampling cup connected with Teflon tubing to an in-line control valve, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of electrical conduit.

The samplers' flow rates were set by connecting a calibrated rotameter to the inlet of the sampler and adjusting the control valve on the sampler so that the flow rate indicated by the rotameter was about 12.4 liters per minute (lpm). The actual flow was then calculated from the rotameter's calibration and reported as the sample collection flow rate.

The flow rate of each sampler was audited with a 30 lpm Matheson mass flow meter traceable to the National Institute of Standards and Technology, following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged -0.6% and ranged from 0% to -1.2% (Table 1).

During the actual sampling period, the flow rate of some samplers dropped considerably, thus making necessary an audit of the rotameter over the full range of flow rates observed. The rotameter was audited on April 6, 1993, and the difference between the reported and the true flow rates averaged -0.8%, and ranged from 0% at 16.2 lpm to -2.0% at 9.6 lpm (Table 2).

Table 1. Results of the flow rate audit of the air samplers used in the monitoring of Carbofuran.

Sampler	Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
1	12.3	16.0	16.0	0
2	12.6	16.4	16.6	-1.2
3	12.5	16.3	16.5	-1.2
4	12.4	16.1	16.1	0
5	12.4	16.1	16.2	-0.6

Table 2. Results of the flow rate audit of the rotameter.

Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
12.4	16.2	16.2	0
12.0	15.6	15.6	0
11.5	14.8	15.0	-1.3
8.0	9.6	9.8	-2.0

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

SYSTEM AUDIT

A system audit of the field and laboratory operations was conducted to evaluate the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation. The audit was conducted by reviewing the method validation data sent to the CARB and through a telephone conversation with Chuck Mourer of the TAL. The following is a discussion of the audit findings.

Sample Handling and Storage

Sampling was conducted by staff of the ARB's EEB, following the schedule specified in the sampling protocol. After sampling, the exposed XAD-4 resin was collected into clean 4-oz glass jars with teflon-lined lids. The samples were stored over dry ice in an ice chest until they were delivered to the laboratory at the end of the sampling period.

Upon receipt at the laboratory, the samples were logged in and stored in a freezer at -20°C. Extraction and analysis of the samples were carried out within three days of receipt.

Sample Analysis

The analytical method was developed by laboratory staff and is described in a document entitled "Pilot Monitoring Study of Two Pesticides in Air." The method entails extraction of the XAD-4 resin with ethyl acetate, evaporation to dryness, addition of 2 ml ethyl acetate, and analysis by gas chromatography (refer to the protocol available in the QA office for further details). Analyses were performed with a Varian Model 6500 gas chromatograph equipped with a thermionic specific nitrogen-phosphorus detector and a Varian Vista Model 402 data system.

The analyses were conducted in duplicate. The calibration standards were prepared within ten days of the date of analysis and had concentrations of 0.12, 0.25, 0.50, and 1.0 ug/ml. The total Carbofuran mass was calculated from the height of the peaks on the chromatogram.

Quality control activities performed to monitor and document the quality of the data included analysis of three laboratory spikes, one method blank, one field blank, and seven duplicate samples. The response factor of the calibration standards was monitored by the analyst to confirm the instrument's stability, but the results were not plotted on a control chart. The study did not include field spikes.

Method Validation

The limit of detection (LOD) was determined as the total mass equivalent to the concentration of the second-lowest calibration standard. The LOD was calculated as 0.375 ng per sample. The laboratory set the limit of quantitation as 0.5 ug per sample.

A trapping efficiency study was conducted by drawing ambient air at 48 to 67 lpm for 24 hours through triplicate assemblies, each consisting of a funnel spiked with 100 ug of Carbofuran, and two sampling cups (primary and secondary) connected in series. At the end of the run, each component was extracted and analyzed separately. The trapping efficiency averaged 90.6%, and no Carbofuran was detected in the secondary sampling cups.

The method recovery rate was determined by spiking resin samples in triplicate with 1.0 ug of Carbofuran. The recovery rates averaged 95%. In a previous study, three pairs of resin samples were spiked with 1, 10 and 100 ug of Carbofuran, and the recoveries averaged 99.2%, 98.7%, and 107.9%, respectively.

Stability studies were conducted by spiking resin samples in triplicate with 1, 10, and 100 ug of Carbofuran and storing them at -20°C for twelve days. The recoveries averaged 107.0%, 110.1%, and 91.7%, respectively.

Documentation

All the samples received at the laboratory were accompanied by ARB's chain-of-custody records. Upon receipt, the samples were inspected and logged into an electronic file . The field sample number of each sample was recorded, and a unique laboratory number was assigned.

Field data sheets containing the sample collection information were retained by the EEB staff. The information included sampler location, date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date of analysis, results, and analyst. The raw analytical data and the results of the analyses were stored in an electronic spreadsheet. Hard copies of the run data and the chromatograms were saved in an accessible form.

LABORATORY PERFORMANCE AUDIT

The accuracy of the TAL's analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with measured amounts of Carbofuran. The samples were prepared on April 15, 1993, following the procedures outlined in Attachment II. The samples were delivered to the laboratory on the same day, and they were extracted and analyzed immediately.

The difference between the assigned and the reported Carbofuran mass averaged -4.0% and ranged from -10.0% to 5.0% (Table 3), which is consistent with the reported method recoveries. The results of duplicate samples indicate a high degree of precision for the method.

Table 3. Results of TAL's analyses of Carbofuran audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
CBF-1	5.0	4.80	-4.0
CBF-2	3.0	3.15	5.0
CBF-3	10.0	9.37	-6.3
CBF-4	3.0	2.84	-5.3
CBF-5	0	<0.5	N/A
CBF-6	5.0	4.50	-10.0
CBF-7	10.0	9.67	-3.3

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

CONCLUSIONS

In general, good quality control practices were observed during the study. The records for field operations were appropriate; the flow rates reported were in good agreement with the actual flow rates measured by the QA staff; the sample handling and storage procedures, the analytical methodology, and the method validation were appropriate; and the results of the analytical performance audit were in excellent agreement with the expected values.

The only deficiencies noticed were the lack of control charts or response factor plots, and the omission of field spikes. A control chart would demonstrate statistical control of the method and document its uncertainty. Response factor plots would allow the analyst to monitor the instrument's sensitivity over time, so that changes such as degradation of the column, the detector, or the standards could be detected. Finally, field spikes should be included with each batch of samples submitted to the laboratory to monitor sample recovery.

ATTACHMENT I

Flow Audit Procedure for Air Samplers Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable Brooks automatic flow calibrator. The audit device is placed in series with the sampler's inlet and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.

2. Calibrated differential pressure gauge with laminar flow element.

3. 1/4" O.D. Teflon tubing.

4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.

2. Connect the outlet port of the sampler's flow control valve to the inlet port of the audit device with a 5 ft. section of Teflon tubing and Swagelock fittings.

3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.

4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.

5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

ATTACHMENT II

Performance Audit Procedure
For The Laboratory Analysis Of Carbofuran

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Carbofuran. The audit is conducted by submitting audit samples spiked with known concentrations of Carbofuran. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Carbofuran, 0.2 mg/ml in Ethyl Acetate, Chem Service #F2006.
2. Ethyl Acetate, nanograde.
3. XAD-4 Resin.
4. Glass Jars, 4 FL OZ, 58-mm diameter.
5. 50 ul Microsyringe.

Safety Precautions

Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only in a well ventilated area, preferably under a fume hood. Wear rubber gloves and protective clothing.

Sample Preparation

Prepare seven audit samples from the 0.2 mg/ml Carbofuran spiking solution according to the following table:

Sample	0.2 mg/ml Carbofuran Volume (ul)
CBF-1	25
CBF-2	15
CBF-3	50
CBF-4	15
CBF-5	0
CBF-6	25
CBF-7	50

1. Measure 30 ml of XAD-4 resin into a glass jar.
2. Transfer the appropriate volume of the Carbofuran spiking solution onto the resin with the syringe, using a circular motion while slowly pushing the plunger. Do not allow the solution to run down the sides of the jar. Touch off any remaining droplets of the solution onto the resin, and shake off any resin adhering to the needle by tapping it gently against the rim of the jar.
3. Cover the jar with the plastic cap provided.
4. Label each jar with its assigned number and store in a freezer until ready for analysis.

Appendix II: Captan Ambient Monitoring Report (ARB/EEB)

State of California

AIR RESOURCES BOARD

Ambient Air Monitoring for Captan in Kern County During Spring, 1993

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C89-041

Report Date: March 22, 1994

APPROVED:

________________, Project Engineer
Testing Section

Peter K. Ouchida, Manager
Testing Section

________________, Chief
Engineering Evaluation Branch

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 Captan in Kern County During Spring, 1993

This report presents the results of ambient air monitoring for captan and its primary breakdown product, tetrahydrophthalimide (THPI) during the month of peak use, in the county of peak use. Samplers were set up in various towns near expected application sites. The results are based on samples collected by the Air Resources Board Engineering Evaluation Branch staff and analyzed by the Trace Analysis Laboratory, Department of Environmental Toxicology at U.C. Davis. No captan or THPI was measured above the minimum detection limits (0.25 ug/sample and 0.5 ug/sample, respectively). Based on the average air sampling volume of 19.4 m^3, these values result in minimum detectable concentrations of 0.013 ug/m^3 for captan and 0.026 ug/m^3 for THPI. The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

LaJuan Taylor and Ken Lewis were the Instrument Technicians. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch as well as the Kern County Agricultural Commissioner's Office. Chemical analyses were performed by the Department of Environmental Toxicology at U.C. Davis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

State of California
Air Resources Board

Ambient Air Monitoring for Captan in Kern County During Spring, 1993

I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a four-week ambient monitoring program for captan and its primary breakdown product, tetrahydrophthalimide (THPI) in Kern County during the Spring of 1993. As required by AB 1807, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

The Pesticide Use Report for 1991 indicates that captan was used mainly on almonds, grapes and strawberries, with lesser amounts used on other crops. The greatest amount of captan was applied in Kern County during July where it is applied primarily on grapes as a fungicide. Statewide, captan is primarily applied on almonds.

II. DESCRIPTION

Captan is a protectant-eradicant fungicide used on various crops. It is a white solid, with a melting point of 175°C. It has very low solubility in organic solvents and is essentially insoluble in water. The vapor pressure is less than 8.00 x 10^{-8} mm Hg at 25°C. The acute oral LD$_{50}$ for rats is 10,000 mg/kg. Captan is regulated as a restricted use material under section 6400, Title 3 of the California Code of Regulations.

III. SAMPLING LOCATIONS

The 1991 Pesticide Use Report (PUR) was used to determine areas of high usage and peak periods of application. This information along with the recommendations of the Kern County Office of Agricultural Commissioner were used to determine which locations would be expected to be near captan applications. As a result four sites were selected: one in Arvin (site A), one in Lamont (site M), one in Edison (site E) and one in Bakersfield (site BF). TABLE I lists the sample identifications and FIGURE I shows the location of these sampling sites. In addition, a "rover" was moved among the sampling sites to obtain duplicate collocated samples which were used to evaluate the precision of the data.

The sites were chosen on the basis of the criterion listed in the QA Plan for Pesticide Monitoring (APPENDIX I). Other considerations in selecting the monitoring sites were: proximity to expected applications 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 bed of XAD-4 resin (see APPENDIX II). The holder was made of Teflon and contained approximately 30 cc of resin. The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any captan present in the sampled ambient air was captured by the XAD-4 adsorbent. Subsequent to sampling, the resin was transported on dry ice to the Trace Analysis Laboratory (TAL), Department of Environmental Toxicology (DET), U.C. Davis for analysis.

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

The sample pump was started and the flow through the holder was adjusted with a metering valve to an indicated reading of 16.0 on a flow meter. This was accomplished by attaching a calibrated flow meter to the inlet of the resin holder. 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 16.0 and was recorded (if different from the planned lpm) along with date, time and site location. Calibration prior to use in the field indicated that an average flow rate of 14.85 liters per minute (lpm) was actually achieved when the flow meter was set to 16.0. Samples were run at this rate for approximately 24 hours. Samples were collected Monday through Friday, four samples per week.

At the end of each sampling period the final indicated flow rate (if different than the set 16.0), the stop date, and the stop time were recorded. The XAD-4 resin was then removed from the holder, transferred to a pre-cleaned jar with a Teflon lined lid. An identification label was affixed to the jar. Each jar was then placed in an ice chest containing dry ice until the jars were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the DET staff. The XAD-4 was extracted with 75 ml of ethyl acetate, concentrated, followed by gas chromatography (GC) separation on a DB-5 megabore column and measurement by a thermionic specific (nitrogen/phosphorous) detector (TSD) (APPENDIX III). The minimum detection limit was a signal five times the baseline noise.

VI. RESULTS

Results for captan and THPI are shown in TABLE I and APPENDIX III. Many of the flow rates decreased from the original set value. The reported volumes (TABLE I) were calculated using the average of the beginning and ending flow rates. No captan or THPI was measured above their minimum detection limit (0.25 ug/sample and 0.5 ug/sample, respectively.) Based on the average air sampling volume of 19.4 m^3, these values result in minimum detectable concentrations of 0.013 ug/m^3 for captan and 0.026 ug/m^3 for THPI.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Laboratory Report for captan and THPI (APPENDIX III). TAL also conducted concurrent recovery of spike samples during the analysis of the field samples (APPENDIX III).

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX I) were followed. A system audit and laboratory performance audit were conducted by the Quality Management and Operations Support Branch of the ARB. The results are shown in APPENDIX IV.

TABLE I. Captan Ambient Monitoring Sites

Site ID	Address
E	Edison School 721 Edison Rd. Bakersfield, CA 93307
A	Arvin High School P.O. Box 518 Arvin, CA 93203
M	Mountain View School Mountain View Rd. and Hwy. 184 Lamont, CA 93241
BF	ARB Ambient Monitoring Station 225 Chester Avenue Bakersfield, CA 93301

TABLE II. Captan Ambient Monitoring Data

Sample ID	Time (min.)	Volume (m^3)	Captan Detected (ug)	THPI Detected (ug)	Date
1A-1	1415	21.0*	<0.25	<0.5	5/11/93
1A-2	1415	19.5	<0.25	<0.5	"
1M	1410	20.9*	<0.25	<0.5	"
1E	1415	18.2	<0.25	<0.5	"
1BF	1420	17.1	<0.25	<0.5	"
2A-1	1440	21.4*	<0.25	<0.5	5/12/93
2A-2	1440	18.5	<0.25	<0.5	"
2M	1445	21.5	<0.25	<0.5	"
2E	1435	21.3	<0.25	<0.5	"
2BF	1435	21.3	<0.25	<0.5	"
3A-1	1410	20.9	<0.25	<0.5	5/13/93
3A-2	1410	20.9	<0.25	<0.5	"
3M	1415	21.0	<0.25	<0.5	"
3E	1415	21.0	<0.25	<0.5	"
3BF	1410	20.9	<0.25	<0.5	"
3B	BLANK	--	<0.25	<0.5	"
4A	1430	21.2*	<0.25	<0.5	5/18/93
4M-1	1440	17.8	<0.25	<0.5	"
4M-2	1440	21.4*	<0.25	<0.5	"
4E	1415	20.3*	<0.25	<0.5	"
4BF	1445	19.1	<0.25	<0.5	"
5A	1445	21.5*	<0.25	<0.5	5/19/93
5M-1	1380	18.5	<0.25	<0.5	"
5M-2	1380	20.5*	<0.25	<0.5	"
5E	1440	19.8	<0.25	<0.5	"
5BF	1380	20.5*	<0.25	<0.5	"
6A	1390	17.9*	<0.25	<0.5	5/20/93
6M-1	1390	17.2	<0.25	<0.5	"
6M-2	1390	20.6*	<0.25	<0.5	"
6E	1385	19.1	<0.25	<0.5	"
6BF	1400	20.8	<0.25	<0.5	"
7A	1380	20.5	<0.25	<0.5	5/21/93
7M-1	1380	13.7	<0.25	<0.5	"
7M-2	1380	20.5	<0.25	<0.5	"
7E	1380	20.5	<0.25	<0.5	"
7BF	1360	20.2	<0.25	<0.5	"
7B	BLANK	--	<0.25	<0.5	"
8A	1415	21.0	<0.25	<0.5	5/25/93
8M	1465	21.8*	<0.25	<0.5	"
8E-1	1355	18.2*	<0.25	<0.5	"
8E-2	1355	18.2	<0.25	<0.5	"
8BF	1420	21.1	<0.25	<0.5	"

*Indicates the average of beginning and ending flow rates.

Minimum detection limit = 0.13 ug/m^3 for captan and 0.026 ug/m^3 for THPI based on average air sampling volumes.

TABLE II. Captan Ambient Monitoring Data (cont.)

Sample ID	Time (min.)	Volume (m^3)	Captan Detected (ug)	THPI Detected (ug)	Date
9A	1390	20.6	<0.25	<0.5	5/26/93
9M	1395	17.9*	<0.25	<0.5	"
9E-1	1390	16.6	<0.25	<0.5	"
9E-2	1390	20.6	<0.25	<0.5	"
9BF	1380	20.5	<0.25	<0.5	"
10A	1380	20.5	<0.25	<0.5	5/27/93
10M	1380	16.6*	<0.25	<0.5	"
10E-1	1380	16.6*	<0.25	<0.5	"
10E-2	1380	20.5	<0.25	<0.5	"
10BF	1380	20.5	<0.25	<0.5	"
11A	1280	19.0	<0.25	<0.5	5/28/93
11M	1230	18.3	<0.25	<0.5	"
11E-1	1340	18.0*	<0.25	<0.5	"
11E-2	1340	18.0*	<0.25	<0.5	"
11BF	1275	18.9	<0.25	<0.5	"
11B	BLANK	--	<0.25	<0.5	"
12A	1350	20.0	<0.25	<0.5	6/2/93
12M	1340	19.9	<0.25	<0.5	"
12E-1	1340	19.9	<0.25	<0.5	"
12E-2	1340	19.9	<0.25	<0.5	"
12BF	1345	16.7*	<0.25	<0.5	"
13A	1290	19.2	<0.25	<0.5	6/3/93
13M	1290	16.0*	<0.25	<0.5	"
13E-1	1290	16.6*	<0.25	<0.5	"
13E-2	1290	19.2	<0.25	<0.5	"
13BF	1280	19.0	<0.25	<0.5	"
13B	BLANK	--	<0.25	<0.5	"
14A	1310	16.2*	<0.25	<0.5	6/4/93
14M	1320	14.7*	<0.25	<0.5	"
14E-1	1335	19.8	<0.25	<0.5	"
14E-2	1335	18.4*	<0.25	<0.5	"
14BF	1350	20.0	<0.25	<0.5	"

*Indicates the average of the beginning and ending flow rates.

Minimum detection limit = 0.13 ug/m^3 for captan and 0.026 ug/m^3 for THPI based on average air sampling volumes.

Figure I. Captan Monitoring Area

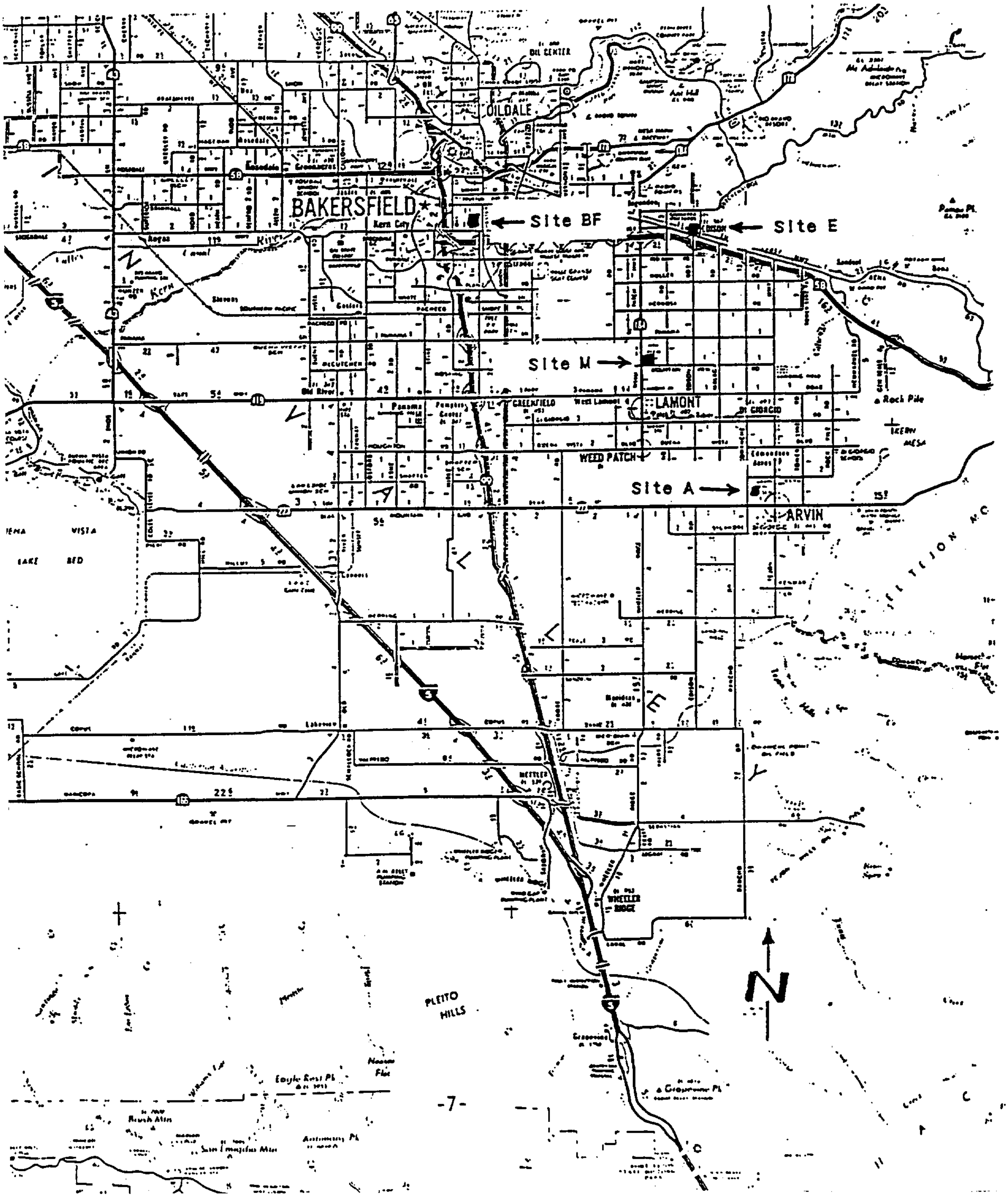
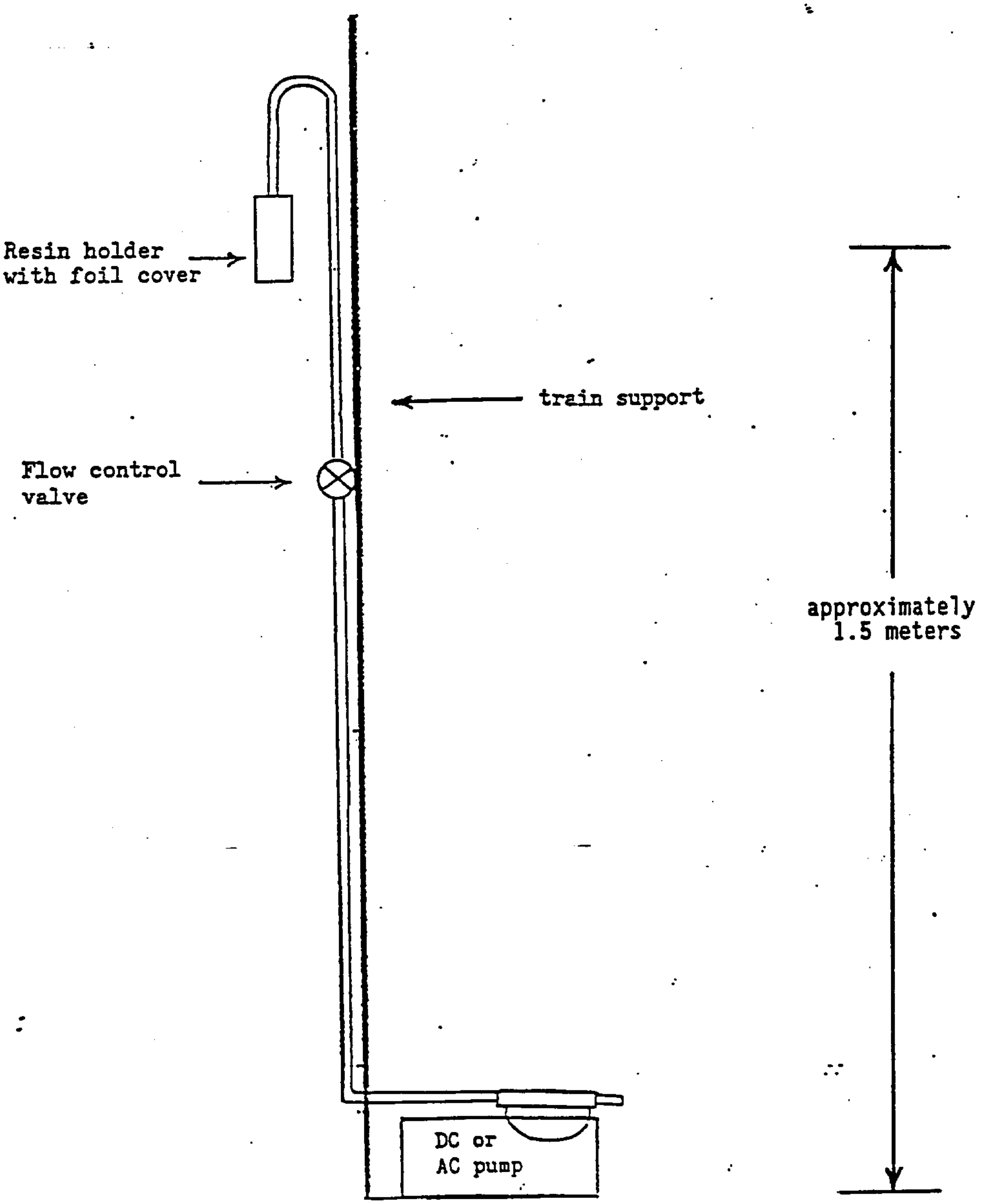


Figure II. Captan Monitoring Apparatus



APPENDIX I.

QUALITY ASSURANCE PLAN

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN
FOR PESTICIDE MONITORING

Prepared by the

Monitoring and Laboratory Division

and

Stationary Source Division

Revised: February 4, 1994

APPROVED:

Genevieve Shiroma, Chief
Toxic Air Contaminant
Identification Branch

Cook, Chief
Quality Management and Operations
Support Branch

George Lew, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signifiy 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.

TABLE OF CONTENTS

Page

APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for **ambient** pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide **application** for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the **application** samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.
2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).
3. Specification of sampling periods and flow rates.
4. Description of the analytical method.
5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

   A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

   Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

   The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

   Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

   The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

   All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: ______________ Date: ____/____/____
Sample/Run #: ______________ Time: ______________
Job name: ______________
Sample Location: ______________
Type of Sample: ______________
Log #'s: ______________

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: ______________

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX II.

SAMPLING PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

Captan Monitoring in Kern County during Spring, 1993

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C89-041

Date: April 12, 1993

APPROVED:

D. Fitzell, Project Engineer
Testing Section

Peter K. Ouchida, Manager
Testing Section

George Lew, Chief
Engineering Evaluation Branch

Protocol for Captan Monitoring
in Kern County during Spring, 1993

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) will conduct a 3-day source impacted ambient monitoring program upwind and downwind of an application of captan as well as a four week ambient study to determine possible exposure to population centers near the site of applications. Captan is a protectant-eradicant fungicide used on grapes, almonds, stone fruits and apples. The primary breakdown product, tetrahydrophthalimide (THPI) will also be monitored. A report on the measured concentrations of both will be submitted to DPR.

II. Sampling

A stainless steel valve down stream of the sampling medium will be used to control all sample flow rates. The flow rate will be set and checked with a calibrated flowmeter. Captan and its breakdown product, THPI, will be collected on a bed of XAD-4 resin. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. Any change in the flow rates will be recorded in a log book, along with any other pertinent information.

A. Application

Prior to application, background samples will be taken to establish if any captan is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Samples will be collected with DC-powered pumps capable of flows of approximately 16 liters per minute. Sample collection will follow the timetable outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" as closely as is reasonably possible.

Five samplers will be used; each approximately 15 yards from the perimeter of the field. Four will be placed at the center of each face (assuming a rectangular field) of the field. The fifth sampler will be collocated with one of the other samplers to obtain precision data. These distances and locations are approximate and dependent on the physical obstacles surrounding the field. ARB's "Quality Assurance Plan for Pesticide Monitoring" will be followed as closely as possible.

B. Ambient

In order to determine any possible exposure to major population centers in the county of peak use, four AC powered samplers will be set up in towns near the sites of potential applications. A fifth sampler will be collocated with each of the other samplers at different times throughout the monitoring period for precision data. Samples will be collected at approximately 16 lpm for 24-hour intervals, Monday through Friday for a period of four weeks.

III. Analysis

All samples will be analyzed by the Department of Environmental Toxicology (DET), University of California, Davis. The resin will first be extracted with ethyl acetate to remove both captan and THPI. The captan will be separated on a DB-1 (or similar) column and measured with a Hall detector in the chlorine mode. The analytical procedure for the breakdown product, THPI, has not been finalized at this point. It is expected to use a similar column, but with measurement by a nitrogen-phosphorous detector (NPD).

IV. Quality Assurance

Field sampling and laboratory analytical quality assurance activities are described in the ARB's "Quality Assurance Plan for Pesticide Monitoring."

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. Sample flow rates will be calibrated prior to and after sampling in the field.

A chain of custody sheet will accompany all samples. A field log book will be used to record start and stop times, sample ID's and any other significant data, including field size, application rate, formulation, and length of the application.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers (Instrument Technician).

APPENDIX III.

LABORATORY REPORTS

Refer to Chapter 2 Captan Application and Ambient Monitoring Report (TAL)

APPENDIX IV.

QA/QC AUDIT REPORT

October 22, 1993

AUDIT REPORT

CAPTAN MONITORING IN KERN AND TULARE COUNTIES

SUMMARY

In May of 1993, the Engineering Evaluation Branch of the California Air Resources Board conducted ambient air sampling in Kern and Tulare Counties, California, to document the airborne emissions of Captan and its tetrahydrophthalimide (THPI) breakdown compound during the period of peak applications in Kern County. The samples were analyzed by the Trace Analytical Laboratory of the UC Davis Department of Environmental Toxicology.

On June 8, staff of the Quality Assurance Section of the Air Resources Board conducted an audit of the two rotameters used to set the flow rate of the air samplers. The audits were conducted with a mass flow meter traceable to the National Institute of Standards and Technology. The difference between the reported and true flow rates averaged -2.0% with a range of -4.9% to 1.3% for one rotameter, and -3.0% with a range of -5.9% to 1.7% for the other.

A system audit of the Trace Analytical Laboratory was conducted to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that these were consistent with good practice.

On May 28, seven samples spiked with measured amounts of Captan and THPI were submitted to the laboratory for analysis. The samples were prepared from 99.0% neat Captan and THPI samples obtained from Chem Service. The difference between the assigned and the reported mass averaged 6.3% with a range of 0.9% to 9.5% for Captan, and 6.2% with a range of -2.5% to 11.7% for THPI.

The only deficiencies noticed in the study were the use of an uncertified mass flow meter in the calibration of the rotameters, and the lack of control charts or response factor plots, and field spikes in the analysis of the samples.

AUDIT REPORT

CAPTAN MONITORING IN KERN AND TULARE COUNTIES

INTRODUCTION

In May of 1993, the Engineering Evaluation Branch (EEB) of the California Air Resources Board (CARB) conducted ambient air sampling to document the airborne emissions of Captan and one of its breakdown products, cis-1,2,3,6-tetrahydrophthalimide (THPI), during the period of peak applications in Kern County, California. Samples were collected in populated areas of Kern County, and in the vicinity of a treated field in Tulare County by drawing ambient air at measured rates through sampling cups containing an adsorbant resin. The samples were later analyzed by the Trace Analytical Laboratory (TAL) of the UC Davis Department of Environmental Toxicology. Gabriel Ruiz of the CARB's Quality Assurance (QA) Section conducted an audit of the rotameters used to set the samplers' flow rate, a system audit of the field and laboratory operations, and a performance audit of the analytical method.

FLOW RATE AUDIT

The air samplers consisted of a sampling cup connected with Teflon tubing to an in-line control valve, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Figure 1). The samplers' flow rates were set by connecting a calibrated rotameter of low flow resistance to the inlet of the sampler and adjusting the control valve on the sampler so that the actual flow rate, as calculated from the rotameter's calibration, was 16 liters per minute (lpm).

The flow rate of each sampler was audited individually at the EEB's shop in Sacramento on March 11, 1993, before monitoring was initiated. The audits were conducted with a 30 lpm Matheson mass flow meter (MFM) traceable to the National Institute of Standards and Technology, following the procedures outlined in Attachment I. The difference between the reported and the true flow rates averaged -0.6% and ranged from -1.2% to 0%. The results were presented in the audit report on Carbofuran Monitoring in Imperial County (CARB, June 30, 1993).

The rotameter used to set the sampler flow rates was broken just when monitoring had begun, and was replaced with two rotameters of higher flow resistance. These rotameters were audited on June 8, with the same 30 lpm Matheson MFM used before. Since the indicated flow rates observed in the field actually ranged from 5 to 16 lpm, an attempt was made to cover the entire range in the audit; however, only indicated flow rates up to 13 lpm could be verified, because the capacity of the sampler's pump was not sufficient to overcome the combined flow resistance of the audit device and the rotameter. While the accuracy of the rotameters at flow rates greater than 13 lpm could not be ascertained, the pumps proved capable of sustaining flow rates of 16 lpm in the field.

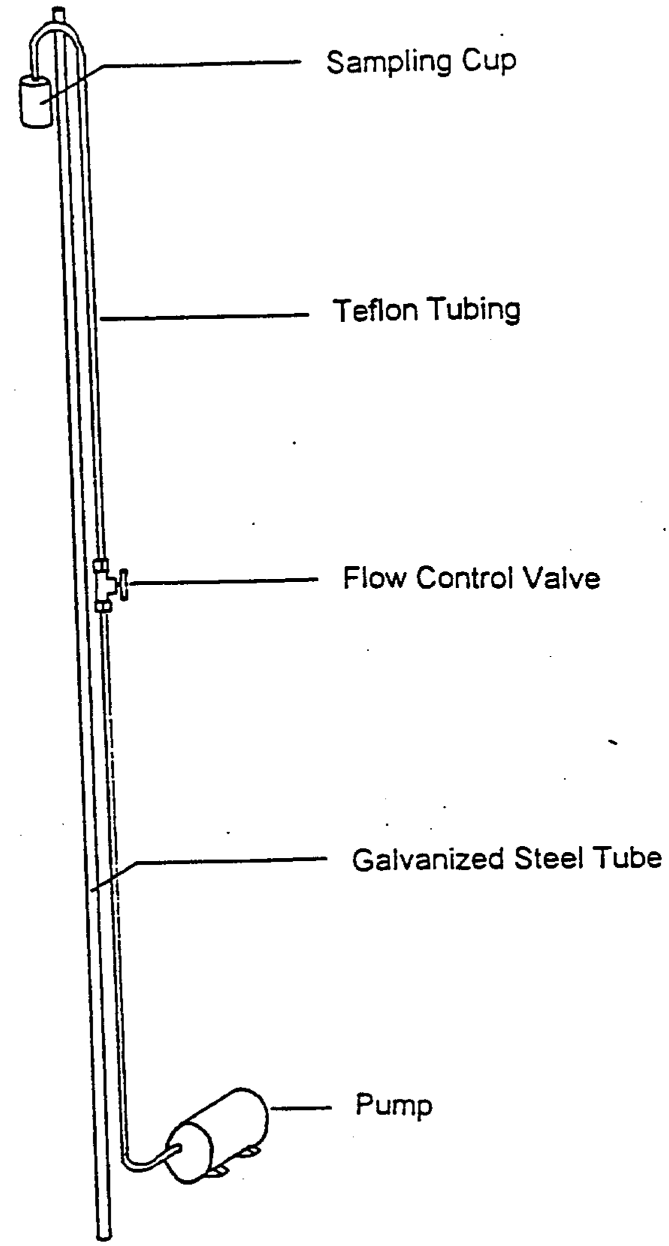


Figure 1. Air sampler used in the monitoring of Captan and THPI.

The difference between the reported and true flow rates averaged -2.0% with a range of -4.9% to 1.3% for the rotameter used in the ambient monitoring (Table 1), and -3.0% with a range of -5.9% to 1.7% for the rotameter used in the application monitoring (Table 2). The reported flow rates were fairly accurate, but an increasingly negative bias was noticed as the flow rates increased from 5 to 13 lpm. The bias was probably caused by the lack of a correction factor for the MFM used in the calibration of the rotameters, since it was uncertified.

Table 1. Results of the audit of the rotameter used to set the sampler flow rates in the ambient monitoring of Captan and THPI.

Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
5.0	5.40	5.33	1.3
6.0	6.54	6.46	1.2
7.0	7.44	7.39	0.7
8.0	8.28	8.41	-1.5
9.0	9.18	9.40	-2.3
10.0	10.08	10.41	-3.2
11.0	10.92	11.43	-4.5
12.0	11.84	12.45	-4.9
13.0	12.87	13.52	-4.8

Table 2. Results of the audit of the rotameter used to set the sampler flow rates in the Captan application monitoring.

Set Flow (lpm)	Reported Flow (lpm)	True Flow (lpm)	Percent Difference
5.0	5.25	5.36	-2.1
6.0	6.66	6.55	1.7
7.0	7.41	7.60	-2.5
8.0	8.52	8.50	0.2
9.0	9.24	9.48	-2.5
10.0	9.93	10.44	-4.9
11.0	10.86	11.49	-5.5
12.0	11.94	12.62	-5.4
13.0	12.69	13.49	-5.9

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

SYSTEM AUDIT

A system audit of the field and laboratory operations was conducted to evaluate the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation. The audit was conducted by reviewing the method validation data sent to the CARB, a visit to the laboratory on May 28, 1993, and telephone conversations with Chuck Mourer and Greg Hall of the TAL. The following is a discussion of the audit findings.

Sample Handling and Storage

Sampling was conducted by staff of the ARB's EEB, following the schedule specified in the sampling protocol. After sampling, the exposed XAD-4 resin was collected into clean 4 fluid-ounce glass jars with teflon-lined lids. The jars were then placed inside cardboard boxes and stored over dry ice in an ice chest until they were delivered to the laboratory on Friday of each week.

Upon receipt at the laboratory, the samples were logged in and stored in a freezer at -20°C. Extraction and analysis of the samples were carried out within one week of receipt.

Sample Analysis

The analytical method was developed by laboratory staff and is described in a document entitled "Pilot Monitoring Study of Two Pesticides in Air." The method entails extraction of the XAD-4 resin with ethyl acetate, evaporation to dryness, addition of 2 ml ethyl acetate, and analysis by gas chromatography (refer to the protocol available in the QA office for further details). Captan analyses were performed with a Varian 6000 chromatograph equipped with a Hall electrolytic detector, and THPI analyses were performed with a Varian 3500 chromatograph equipped with a nitrogen-phosphorus detector.

The calibration standards were prepared within three weeks of analyses and their stability was monitored by periodic laboratory spikes. The total Captan and THPI mass were calculated from the height of the peaks on the chromatogram.

Quality control activities performed to monitor and document the quality of the data included duplicate analyses of all the samples, and analysis of three laboratory spikes per batch of samples, one method blank per batch, one field blank per shipment of samples, and one duplicate sample per sampling day. The response factors of the calibration standards were monitored by the analyst to confirm the instrument's stability, but the results were not plotted on a control chart. The study did not include field spikes.

Method Validation

The limit of detection (LOD) was determined as the total mass equivalent to a peak height of 10 millimeters on the chromatograms, and all the calibration curves were bracketed to include at least one peak in that range. The laboratory set the limit of quantitation as 0.25 ug per sample for Captan, and 0.5 ug per sample for THPI.

Trapping efficiency studies were conducted by drawing ambient air at 40 to 69 lpm for 24 hours through two sets of triplicate assemblies, each consisting of two sampling cups (primary and secondary) connected in series. A plug of glass wool was placed in the primary cup and spiked with 100 ug of Captan or THPI. At the end of the run, each component was extracted and analyzed separately. The trapping efficiency averaged 102% for Captan and 51.7% for THPI. No Captan or THPI were detected in the secondary sampling cups; therefore, it was speculated that the low THPI recoveries were due to chemical breakdown.

The method recovery rate was determined by spiking resin samples in duplicate with 1, 10 and 100 ug of Captan or THPI. The recovery rates averaged 116.0%, 93.6%, and 95.9% for Captan, and 117.0%, 115.0%, and 101.2% for THPI, respectively.

Stability studies were conducted by spiking resin samples in triplicate with 1, 10, and 100 ug of Captan or THPI, and storing them at -20°C for twelve days. The recoveries averaged 111.1%, 102.0%, and 82.3% for Captan, and 121.4%, 112.0% and 102.3% for THPI, respectively.

Documentation

All the samples received at the laboratory were accompanied by ARB's chain-of-custody records. Upon receipt, the samples were inspected and logged into an electronic file. The field sample number of each sample was recorded, and a unique laboratory number was assigned.

Field data sheets containing the sample collection information were retained by the EEB staff. The information included sampler location, date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date of analysis, results, and analyst. The raw analytical data and the results of the analyses were stored in an electronic spreadsheet. Hard copies of the run data and the chromatograms were saved in an accessible form.

LABORATORY PERFORMANCE AUDIT

The accuracy of the TAL's analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with measured amounts of Captan and THPI. The samples were prepared on May 28, 1993, following the procedures outlined in Attachment II. The samples were delivered to the laboratory on the same day, and they were extracted and analyzed immediately.

The difference between the assigned and the reported mass averaged 6.3% with a range of 0.9% to 9.5% for Captan (Table 3), and 6.2% with a range of -2.5% to 11.7% for THPI (Table 4). The results of the duplicate samples indicate a high degree of precision for both methods, and all the results are consistent with the reported method recoveries.

Table 3. Results of TAL's analyses of the Captan audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
CPN-1	5.10	5.38	5.5
CPN-2	3.06	3.26	6.5
CPN-3	0	<0.5	N/A
CPN-4	10.20	10.29	0.9
CPN-5	3.06	3.35	9.5
CPN-6	0	<0.5	N/A
CPN-7	5.10	5.57	9.2

Table 4. Results of TAL's analyses of the THPI audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
CPN-1	3.00	3.35	11.7
CPN-2	5.00	5.10	2.0
CPN-3	0	<0.5	N/A
CPN-4	0	0.5	N/A
CPN-5	5.00	5.52	10.4
CPN-6	10.00	9.75	-2.5
CPN-7	3.00	3.28	9.3

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

CONCLUSIONS

In general, good quality control practices were observed during the study. The records for field operations were appropriate; the flow rates reported were in good agreement with the actual flow rates measured by the QA staff; the sample handling and storage procedures, the analytical methodology, and the method validation were appropriate; and the results of the analytical performance audit were in excellent agreement with the expected values.

The only deficiencies noticed were the use of an uncertified MFM in the calibration of the rotameters, the lack of control charts or response factor plots, and the omission of field spikes. While the reported sample collection flow rates were fairly accurate, the rotameters should have been calibrated with a certified flow measurement device. A control chart would demonstrate statistical control of the method and document its uncertainty. Response factor plots would allow the analyst to monitor the instrument's sensitivity over time, so that changes such as degradation of the column, the detector, or the standards could be detected. Finally, field spikes should be included with each batch of samples submitted to the laboratory to monitor sample recovery.

Flow Audit Procedure for Air Samplers
Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable Brooks automatic flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 V AC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock-fittings.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

ATTACHMENT II

Performance Audit Procedure for the Laboratory Analysis of Captan and THPI

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of Captan and THPI. The audit is conducted by submitting audit samples spiked with known concentrations of Captan and THPI. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Captan, 99.0% pure, Chem Service Lot #30-110B
2. cis-1,2,3,6-Tetrahydrophthalimimde (THPI), 99% pure, Chem Service Lot #55-6NA
3. Ethyl Acetate, nanograde.
4. XAD-4 Resin.
5. Glass Jars, 4 fl. oz., 58-mm diameter.
6. 50 ul Microsyringe.

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Sample Preparation

4 mg/ml Captan Stock Solution: Weigh about 100 mg of Captan into a clean 25 ml volumetric flask. Dissolve with ethyl acetate and dilute to the mark. Record the concentration.

4 mg/ml THPI Stock Solution: Weigh about 100 mg of THPI into a clean 25 ml volumetric flask. Dissolve with ethyl acetate and dilute to the mark. Record the concentration.

0.2 mg/ml Captan Spiking Solution: Transfer 500 ul of the Captan stock solution into a clean 10 ml volumetric flask and dilute with ethyl acetate to the mark. Record the concentration.

0.2 mg/ml THPI Spiking Solution: Transfer 500 ul of the THPI stock solution into a clean 10 ml volumetric flask and dilute with ethyl acetate to the mark. Record the concentration.

Prepare seven audit samples from the 0.2 mg/ml Captan and THPI spiking solutions according to the following table:

Sample	0.2 mg/ml Captan Volume (ul)	0.2 mg/ml THPI Volume (ul)
CPN-1	25	15
CPN-2	15	25
CPN-3	0	0
CPN-4	50	0
CPN-5	15	25
CPN-6	0	50
CPN-7	25	15

1. Measure 30 ml of XAD-4 resin into seven glass jars and label them CPN-1 to CPN-7.
2. Transfer the appropriate volume of the Captan and THPI spiking solutions onto the resin with the syringe, using a circular motion while slowly pushing the plunger. Do not allow the solution to run down the sides of the jar. Touch off any remaining droplets of the solution onto the resin, and shake off any resin adhering to the needle by tapping it gently against the rim of the jar.
3. Cover the jars with the plastic caps provided and store them in a freezer until ready for analysis.

Appendix III: Captan Application Monitoring Report (ARB/EEB)

State of California

AIR RESOURCES BOARD

Ambient Air Monitoring for Captan in Tulare County During Spring 1993, After an Application to a Vineyard

Engineering Evaluation Branch

Monitoring and Laboratory Division

Test Report No. C89-041A

Report Date: March 22, 1994

APPROVED:

______________, Project Engineer
Testing Section

______________, Manager
Testing Section

______________, Chief
Engineering Evaluation Branch

Ambient Air Monitoring for Captan in Tulare County During Spring 1993, After an Application to a Vineyard

This report presents the results of ambient air monitoring for Captan and its primary breakdown product, tetrahydrophthalimide (THPI) after a ground application at a selected vineyard in Tulare County. Detected concentrations of Captan varied from 0.03 to 0.47 ug/m^3. No THPI above the limit of detection (0.5 ug/sample) was found. The results are based on samples collected by the Air Resources Board Engineering Evaluation Branch staff and analyzed by the Trace Analytical Laboratory, Department of Environmental Toxicology at U.C. Davis. The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

LaJuan Taylor was the Instrument Technician. Frankie Martin of V.B. Zaninovich & Sons arranged for a suitable vineyard to monitor. Lynn Baker and Ruth Tomlin of the Air Resources Board Toxic Air Contaminant Identification Branch provided assistance as well as the Kern County Agricultural Commissioner's Office. Chemical analyses were performed by the Trace Analysis Laboratory, Department of Environmental Toxicology at U.C. Davis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

State of California
Air Resources Board

Ambient Air Monitoring for Captan in Tulare County During Spring 1993, After an Application to a Vineyard

I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a three-day source impacted ambient monitoring program for Captan in Tulare County during the Spring of 1993. As required by AB 1807, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

The Pesticide Use Report for 1991 indicates that Captan was used mainly on almonds, grapes and strawberries, with lesser amounts used on other crops. The greatest amount of Captan was applied in Kern County during July where it is applied primarily on grapes as a fungicide. Statewide, Captan is primarily applied on almonds.

II. DESCRIPTION

Captan is a protectant-eradicant fungicide used on various crops. It is a white solid with a melting point of 175°C. It has very low solubility in organic solvents and is essentially insoluble in water. The vapor pressure of Captan is less than 8.00×10^{-8} mm Hg at 25°C. The acute oral LD_{50} for rats is 10,000 mg/kg. Captan is regulated as a restricted use material under Section 6400, Title 3 of the California Code of Regulations.

III. SAMPLING LOCATIONS

A vineyard (Section 19, Township 24S, Range 27E) of about 18 acres was selected (FIGURE I) by Frankie Martin of V.B. Zaninovich & Sons and approved by ARB staff to use for application monitoring. Five samplers were set up: (1) two (collocated) approximately 20 yards south of the field, (2) one approximately 20 yards north of the field (3) one approximately 20 yards east of the field and (4) one approximately 20 yards west of the field. A meteorological station was set up near the eastern sampler (FIGURE II).

The application was by ground and took about forty-five minutes. The fungicide was applied using four tractors; two applying from the north and two applying from the south. The application rate was 3.89 pounds of Captan and 11 ounces of Latron 3-1956 spreader/sticker in 275 gallons of water per acre.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through XAD-4 resin (see APPENDIX I). The holders were made of Teflon and contained approximately 30 cc of resin. The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any Captan present in the sampled ambient air was captured by the XAD-4 adsorbent. Subsequent to sampling, the resin was transported on dry ice to the Trace Analytical Laboratory (TAL) of the Department of Environmental Toxicology (DET), U.C. Davis for analysis.

Sampling trains designed to operate continuously were set up at the sampling sites identified in FIGURE II. Duplicate samples were obtained from the site designated "S." Resin was changed, as closely as practical, according to the schedule outlined in the QA Plan for Pesticide Monitoring (APPENDIX II).

Each sample train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, train support, and a 12VDC battery-powered vacuum pump. A diagram of the sampling train is shown in FIGURE III. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through the resin holder adjusted with a metering valve to an indicated reading of 16.0 on a flow meter. This was accomplished by attaching a calibrated flow meter to the inlet of the resin holder. 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 16.0 and was recorded (if different from the planned lpm) along with date, time and site location. Calibration prior to use in the field indicated that an average flow rate of 14.85 liters per minute (lpm) was actually achieved when the flow meter was set to 16.0.

At the end of each sampling period the final indicated flow rate (if different than the set 16.0), the stop date and the stop time were recorded. The XAD-4 resin was then removed from the holder and transferred to a pre-cleaned jar with a Teflon-lined lid. An identification label was affixed to each jar. Each jar was then placed in an ice chest containing dry ice until the jars were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the TAL, DET staff. The XAD-4 was extracted with 75 ml of ethyl acetate, concentrated, followed by gas chromatography (GC) separation on a DB-5 megabore column and measurement by a Thermionic Specific (nitrogen/phosphorous) Detector (TSD) (APPENDIX III). The minimum detection limit was a signal five times the baseline noise.

VI. RESULTS

Prior to sampling, it was noted that the vineyard was posted for a previous application of Thiodan (Endosulfan) which is used as an insecticide. The TAL at U.C. Davis did not report any interferences caused by this earlier application.

Results for Captan are shown in TABLE I and APPENDIX III. As can be seen from APPENDIX III, no THPI was found above the detection limit. Many of the flow rates decreased from the original set values. The reported values (TABLE I) were calculated using the average of the concentrations determined by using the beginning and ending flow rates independently. The ± values indicate the minimum and maximum concentrations possible using the minimum and maximum flow rates. TABLE II is a summary of the meteorological data collected on site. TABLE III is a pictographic summary of both the meteorological and sampling data. As TABLE I shows, very little Captan was detected. The values ranged from 0.03 to 0.47 ug/m^3 with three of the four values above the detection limit found during the application.

Because the anemometer of the weather station was not working during most of the sampling period, the meteorological data obtained from the nearest California Irrigation Management Information System (CIMIS) location, Visalia, is included as APPENDIX IV.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Laboratory Reports for Captan (APPENDIX III).

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX II) were followed. The Quality Management and Operations Support Branch (QMOSB) of the ARB conducted a flow audit of the samplers as well as a laboratory audit of the DET at U.C. Davis. This report is included as APPENDIX V.

TABLE I. Captan Application Monitoring Data

Sample ID	Time (min.)	Volume (m^3)* min.	Volume (m^3)* max.	Detected (ug)	Concentration** (ug/m^3)	Collection Date (Approx.)
0S-1	275	3.49	4.08	<0.5	--	
0S-2	275	4.08	4.08	<0.5	--	
0E	275	4.08	4.08	<0.5	--	(Background)
0N	280	4.16	4.16	<0.5	--	5/24/93
0W	285	4.23	4.23	<0.5	--	1300-1800
1S-1	110	0.58	1.63	0.30	0.35±.17	
1S-2	110	0.82	1.63	<0.25	--	
1E	120	1.19	1.78	0.41	0.28±.06	(Application)
1N	130	0.96	1.93	<0.25	--	5/25/93
1W	135	2.00	2.00	0.94	0.47	0500-0730
2S-1	115	1.14	1.71	<0.25	--	
2S-2	115	1.56	1.71	<0.25	--	
2E	115	1.71	1.71	<0.25	--	
2N	110	1.63	1.63	<0.25	--	
2W	105	0.78	1.56	<0.25	--	5/25/93
2B	BLANK	--		<0.25	--	0730-0930
3S-1	235	2.81	3.49	<0.25	--	
3S-2	235	3.49	3.49	<0.25	--	
3E	240	3.56	3.56	>0.25	--	
3N	240	3.56	3.56	<0.25	--	5/25/93
3W	235	2.55	3.49	<0.25	--	0930-1330
4S-1	275	4.08	4.08	<0.25	--	
4S-2	275	4.08	4.08	<0.25	--	
4E	270	4.01	4.01	<0.25	--	
4N	270	4.01	4.01	<0.25	--	5/25/93
4W	270	4.01	4.01	<0.25	--	1330-1800
5S-1	755	8.20	11.2	<0.25	--	
5S-2	755	9.01	11.2	<0.25	--	
5E	755	5.59	11.2	<0.25	--	
5N	765	9.71	11.4	<0.25	--	5/25-26/93
5W	765	5.67	11.4	0.25	0.03+.01	1800-0630
6S-1	1435	15.1	21.3	<0.25	--	
6S-2	1435	12.7	21.3	<0.25	--	
6E	1435	15.1	21.3	<0.25	--	
6N	1425	18.9	21.2	<0.25	--	5/26-27/93
6W	1425	17.4	21.2	<0.25	--	0630-0630
7S-1	1455	21.60	21.60	<0.25	--	
7S-2	1455	19.94	21.60	<0.25	--	
7E	1455	20.12	21.61	<0.25	--	
7N	1455	17.88	21.61	<0.25	--	5/27-28/93
7W	1455	15.84	21.61	<0.25	--	0630-0630

*Min. and max. values based on minimum (end of sampling period) and maximum (beginning of sampling period) flow rates.

**± values indicate min. and max. values possible if flow rates were maintained for the whole sampling period.

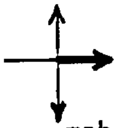
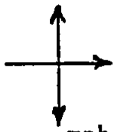
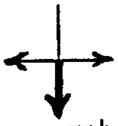
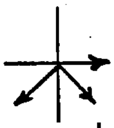
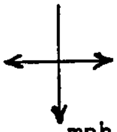
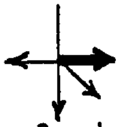
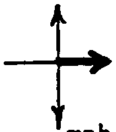
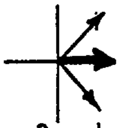
TABLE II. Captan Application Meteorological Data

Sampling Period	Wind* Direction	Wind Speed** (mph)
0	W/S/N	-
1	N/E/W	-
2	N/E/W	-
3	W/S/N	-
4	W/S/N	-
5	W/NW/NE	-
6	W/NW/N/E	3
7	W/NW/SW	3

*Indicates direction wind is blowing from.

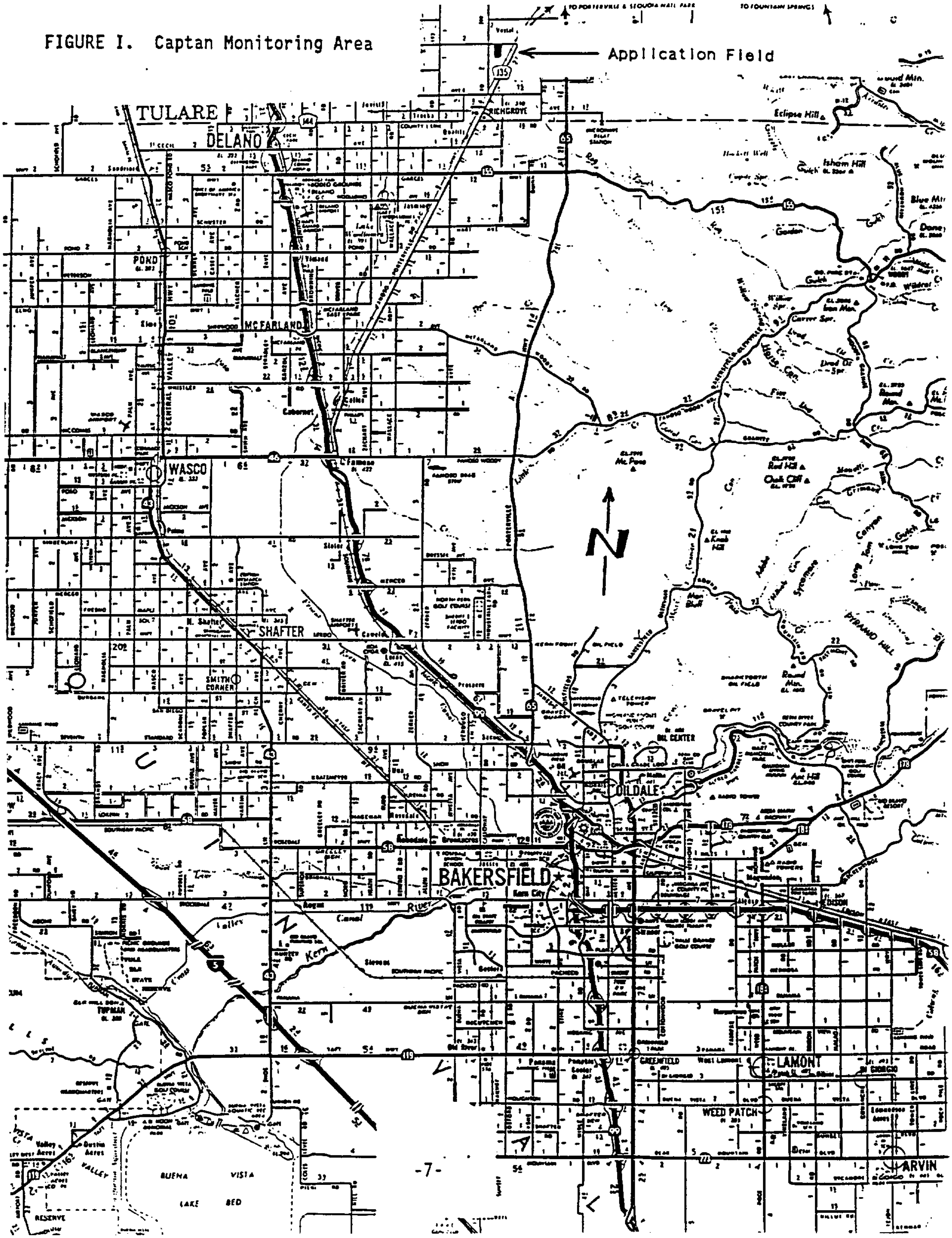
**- indicates anemometer on weather station not working.

Table III. Summary of Captan Application Data (ug/m^3)

ND [N] (0) ND [W]  ND [E] - mph ND [S]	ND [N] (4) ND [W]  ND [E] - mph ND [S]
ND [N] (1) 0.47 [W]  0.28 [E] - mph 0.35 [S]	ND [N] (5) 0.03 [W]  ND [E] - mph ND [S]
ND [N] (2) ND [W]  ND [E] - mph ND [S]	ND [N] (6) ND [W]  ND [E 3 mph ND [S]
ND [N] (3) ND [W]  ND [E] - mph ND [S]	ND [N] (7) ND [W]  ND [E 3 mph ND [S]

( ) indicates sampling period. [ ] indicates sampling site represented.
ND = not detected, less than 0.3 ug/sample
Arrow indicates direction wind is blowing <u>toward</u>.
Bold arrow indicates predominant wind direction.
- indicates anemometer on weather station not working.

FIGURE I. Captan Monitoring Area



Application Field

FIGURE II. Captan Monitoring Sites

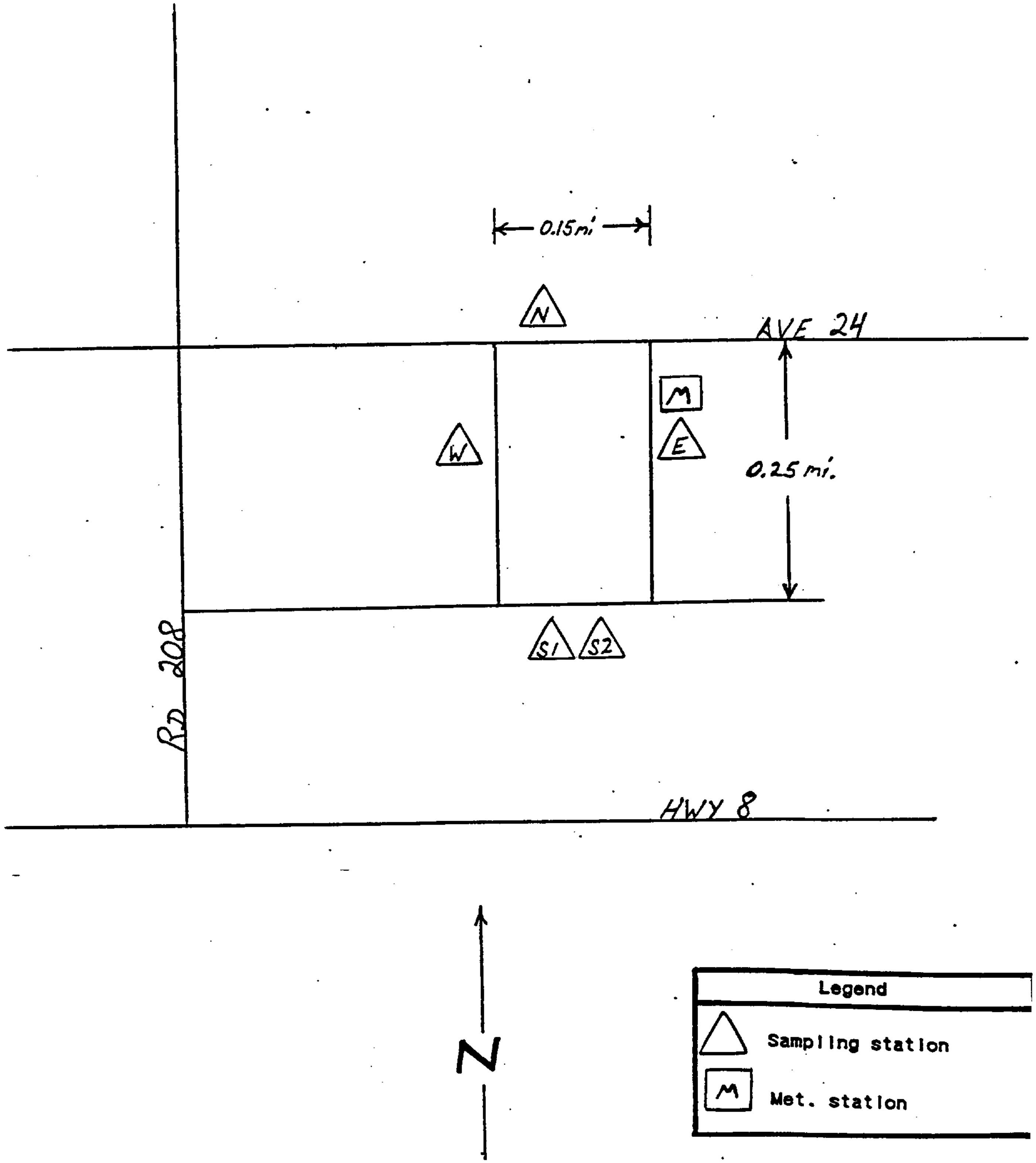


FIGURE III. Captan Monitoring Apparatus