

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

AMBIENT AIR MONITORING FOR MITC IN KERN COUNTY DURING SUMMER 1993

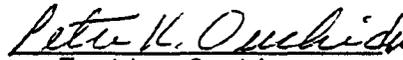
Engineering Evaluation Branch  
Monitoring and Laboratory Division

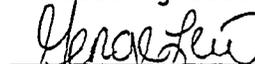
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APPROVED:

  
\_\_\_\_\_, Project Engineer  
Testing Section

  
\_\_\_\_\_, Manager  
Testing Section

  
\_\_\_\_\_, Chief  
Engineering Evaluation Branch

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## Ambient Air Monitoring for MITC in Kern County During Summer 1993

This report presents the results of ambient air monitoring for methyl isothiocyanate (MITC), the primary breakdown product of metam sodium, during a period of high use, in the county of peak use. Samplers were set up in various towns near expected application sites. The results are based on (approximately) 24-hour samples collected by the Air Resources Board Engineering Evaluation Branch staff and analyzed by the Environmental Health Laboratory Branch, Department of Health Services. MITC values ranged from not detected (less than  $0.01 \text{ ug/m}^3$  for a 24-hour sample) to a maximum of 18.  $\text{ug/m}^3$ . The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

## Acknowledgments

Jack Rogers and Jack LaBrue 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 Environmental Health Laboratory Branch, Department of Health Services.

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I. INTRODUCTION

The Air Resources Board (ARB) Engineering Evaluation Branch (EEB) conducted a two-week ambient monitoring program to determine the effects of metam sodium applications in Kern County during the month of July 1993. The effects of the metam sodium applications were determined by measuring the amounts of methyl isothiocyanate (MITC), the primary breakdown product, which has pesticidal activity, acts as a fumigant and is found in the air. Monitoring for carbon disulfide did not occur because the levels expected were below the detection limit of the laboratory. This monitoring was performed at the request of the Office of Environmental Health Hazard Assessment (OEHHA), the California Department of Pesticide Regulation (DPR), and the ARB Toxic Air Contaminant Identification Branch (TACIB).

The purpose of this monitoring program was to determine ambient MITC concentrations when metam sodium use was high under warm air and soil conditions. This was a follow-up to a "best case" (cool air, cool soil temperatures) injection application monitoring which occurred in Brentwood, CA during March 1993.

The Pesticide Use Report for 1991 indicates metam sodium is most widely used (1,395,942 pounds) prior to planting carrots. Heaviest use occurs during August through December in Kern County.

II. DESCRIPTION

Metam sodium (molecular weight 129.18 g/mole) is a soil fumigant used as a fungicide, herbicide, insecticide and nematicide. It has an unpleasant odor, similar to that of carbon disulfide. It is soluble in water (72.2 g/100 ml), moderately soluble in alcohol and sparingly soluble in other solvents. Application is by soil injection or sprinkler irrigation. Metam sodium rapidly breaks down in the presence of water into methyl isothiocyanate (MITC), which has pesticidal activity. Metam sodium is not regulated as a restricted use material under section 6400, Title 3 of the California Code of Regulations.

MITC is a crystalline substance (m.p. 35-36°C, b.p. 119°C) with a molecular weight of 73.12. It is slightly soluble in water and freely soluble in alcohol and ether (Merck Index, Eleventh Edition, 1989).

Lethality values for MITC range from 29 mg/m<sup>3</sup> (LC<sub>100</sub>, rat 30-minute exposure) to 1900 mg/m<sup>3</sup> (LC<sub>50</sub>, rat 1-hour exposure) ("Evaluation of the

Health Risks Associated with the Metam Sodium Spill in the Upper Sacramento River," External Review Draft, OEHHA, September 1992). This wide range indicates the uncertainty of the lethality values. The most sensitive toxicity end point, eye irritation, was reported in cats exposed to 0.2 mg/m<sup>3</sup> MITC for 4 hours. Based on that study, OEHHA set a 24-hour action level for eye irritation of 0.1 ppb (0.3 ug/m<sup>3</sup>). Studies are underway to refine the odor threshold and eye irritation levels for humans.

### 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 metam sodium applications. As a result four sites were selected. All samplers (FIGURE II) were placed on the roofs of the locations. All were single story buildings except for site BF (3 stories). The locations were: one in Weed Patch (site V), one in Lamont (site M), one in Shafter (site R) and one in Bakersfield (site BF). FIGURE I shows the location of these monitoring sites and the sample identifications. TABLE I identifies the sites and gives the addresses. Duplicates were taken at each location although not all duplicates were analyzed.

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 charcoal tubes (APPENDIX II). These tubes are 8 mm x 110 mm, with 400 mg in the primary section and 200 mg in the secondary (SKC catalog #226-09). Any MITC present in the sampled ambient air is captured by the charcoal adsorbent contained in the tubes. Subsequent to sampling, the tubes were stored on dry ice and transported in a container with blue ice to the Environmental Health Laboratory Branch (EHLB) in Berkeley for analysis.

Sampling trains designed to operate continuously were set up at the four sampling sites identified in FIGURE I. Duplicate samples were obtained from all four sites. Sample tubes were changed approximately every twenty-four hours and collected Tuesday through Friday.

Each sample train consisted of a charcoal tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a 115VAC powered vacuum pump. A diagram of the sampling train is shown in FIGURE II. Each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction

of flow. Covers were placed around the tube to protect the adsorbent and any collected material from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration prior to use in the field indicated that an average flow rate of 1.91 lpm was actually achieved when the rotometers were set to 2.0 lpm. This average flow rate was used to calculate all sample volumes.

At the end of each sampling period the final indicated flow rate (if different than the set 2.0 lpm), the stop date and time were recorded. The charcoal tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with dry ice in a covered chest until the tubes were delivered to the laboratory for analysis.

#### V. ANALYTICAL METHODOLOGY

The charcoal tubes recovered from each sampler were analyzed by the EHLB staff. The charcoal in the primary and secondary section of each sample tube was extracted with carbon disulfide followed by gas chromatography (GC) separation on a DB-5 capillary column and measurement by a nitrogen/phosphorous detector (NPD), see APPENDIX III. All samples were analyzed within two weeks of the collection date. Confirmation was performed on the already extracted samples by EHLB staff using gas chromatography/mass spectroscopy (GC/MS). The California Department of Food and Agriculture (CDFA) laboratory used GC/NPD for analysis of some of the duplicate charcoal tube samples (TABLE II).

#### VI. RESULTS

Complete results for MITC are shown in TABLE III and a summary of the results in TABLE IV. The laboratory data is presented in APPENDIX IV. None of the values have been corrected for recovery levels of spiked samples. The average recovery of the spiked samples presented in TABLE III is 65%, indicating the actual values are probably nearly twice the reported values.

A comparison of the QA/QC data presented in TABLE II reveals significantly lower levels detected by the CDFA laboratory compared to the EHLB results. It must be noted that the CDFA laboratory did not analyze their duplicate samples until two months after EHLB.

All flow rates remained constant at 1.91 lpm. The values ranged from not detected (less than  $0.01 \text{ ug/m}^3$  for a 24-hour sample) to  $18 \text{ ug/m}^3$ .

## VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Analytical Procedure for MITC (APPENDIX III). In addition, the EHLB provided field spikes during the monitoring. The samples designated "S" were set out at the same time as the corresponding "BF" sample, but without any air being drawn through it. Thus it was at the same temperature as an actual sample for the same length of time. Recoveries for tubes spiked at 1.0 ug ranged from 0.504 ug to 0.688 ug. The samples designated as "C" were kept on dry ice for the full week, then treated as a normal sample. The recoveries for these two samples also spiked at 1.0 ug were 0.745 ug and 0.565 ug.

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX I) were followed, except only two weeks of monitoring was possible for this study rather than four weeks. All samples were stored on dry ice or in a freezer except for transportation to the laboratory or transportation to the field in the case of the samples labeled "C", when blue ice was used. Spikes were prepared by the Quality Management and Operations Support Branch of the ARB. The results are shown in APPENDIX V.

TABLE I. MITC Ambient Monitoring Sites

Site ID	Address
R	Richland School District Office 331 Shafter Avenue Shafter, CA 93263
BF	ARB Ambient Monitoring Station 225 Chester Avenue Bakersfield, CA 93301
M	Mountain View School Mountain View Rd. and Hwy. 184 Lamont, CA 93241
V	Vineland School 14713 Weedpatch Hwy. Bakersfield, CA 93307

Table II. QA/QC Data (GC/NPD)

Sample ID	CDFA* Results (ug)	EHLB** Results (ug)
1BF	0.59	1.16
1V	4.03	6.42
2M	1.77	2.85
2BF	0.48	0.815
4V	45.39	47.7
4R	ND	0.075
4B	ND	ND
Blank	ND	ND
5ug Spike	4.30	not analyzed

\* Minimum detection limit 0.2 ug/sample. Samples analyzed Oct. 20, 1993.

\*\* Minimum detection limit 0.030 ug/sample. Samples analyzed July 28-31, 1993.

R = Shafter site, BF = Bakersfield site, M = Lamont site and V = Weed Patch site.

TABLE III. MITC Ambient Monitoring Data

Sample ID	Time (min.)	Volume (m <sup>3</sup> )	Detected (ug)	Concentration		Collection Date
				(ug/m <sup>3</sup> )	(ppb)	
1R	1455	2.8	1.11	0.40	0.13	7/20/93
1BF	1365	2.6	1.16	0.45	0.15	"
1M	1365	2.6	2.56	0.98	0.33	"
1V	1360	2.6	6.42	2.5	0.84	"
1S	1.0 ug SPIKE*		0.667	--	--	"
2R	1375	2.6	ND	--	--	7/21/93
2BF	1380	2.6	0.815	0.31	0.10	"
2M	1375	2.6	2.85	1.1	0.37	"
2V	1440	2.8	5.35	1.9	0.64	"
2S	1.0 ug SPIKE*		0.686	--	--	"
2B	BLANK		ND	--	--	"
3R	1380	2.6	5.62	2.2	0.74	7/22/93
3BF	1380	2.6	15.2	5.8	1.9	"
3M	1375	2.6	26.4	10.	3.3	"
3V	1375	2.6	32.0	12.	4.0	"
3S	1.0 ug SPIKE*		0.685	--	--	"
4R	1355	2.6	0.075	0.029	0.0097	7/23/93
4BF	1365	2.6	15.7	6.0	2.0	"
4M	1370	2.6	43.1	17.	5.7	"
4V	1370	2.6	47.7	18.	6.0	"
4S	1.0 ug SPIKE*		0.657	--	--	"
4C	1.0 ug SPIKE**		0.745	--	--	"
4B	BLANK		ND	--	--	"

\* All spikes prepared the same day and stored in a freezer or on dry ice.

\*\* Trip spike carried on dry ice all week.

ND = not detected, <0.030 ug/sample (less than 0.01 ug/m<sup>3</sup> for a 24-hour sample.)

R = Shafter site, BF = Bakersfield site, M = Lamont site and V = Weed Patch site.

$$\text{ppbv} = (\text{ug/m}^3) \times \frac{(8.21 \times 10^{-2} \text{ liter-atm/mole} \cdot \text{K})(298 \text{ K})}{(73.12 \text{ gram/mole})(1 \text{ atm})} = 0.3346 \times (\text{ug/m}^3)$$

TABLE III. MITC Ambient Monitoring Data (Cont.)

Sample ID	Time (min.)	Volume (m <sup>3</sup> )	Detected (ug)	Concentration		Collection Date
				(ug/m <sup>3</sup> )	(ppb)	
5R	1520	2.9	ND	--	--	7/27/93
5BF	1440	2.8	5.96	2.1	0.70	"
5M	1385	2.6	20.3	7.8	2.6	"
5V	1345	2.6	27.9	11.	3.7	"
5S	1.0 ug SPIKE*		0.815	--	--	"
6R	1410	2.7	ND	--	--	7/28/93
6BF	1585	2.6	2.39	0.92	0.31	"
6M	1370	2.6	14.9	5.7	1.9	"
6V	1375	2.6	26.1	10.	3.3	"
6S	1.0 ug SPIKE*		0.601	--	--	"
6B	BLANK		ND	--	--	"
7R	1350	2.6	ND	--	--	7/29/93
7BF	1355	2.6	0.895	0.34	0.11	"
7M	1360	2.6	1.11	0.43	0.14	"
7V	1365	2.6	7.91	3.0	1.0	"
7S	1.0 ug SPIKE*		0.548	--	--	"
8R	1350	2.6	0.182	0.070	0.023	7/30/93
8BF	1350	2.6	3.03	1.2	0.40	"
8M	1365	2.6	11.6	4.5	1.5	"
8V	1355	2.6	21.8	8.4	2.8	"
8S	1.0 ug SPIKE*		0.549	--	--	"
8C	1.0 ug SPIKE**		0.565	--	--	"
8B	BLANK		ND	--	--	"

\* All spikes prepared the same day and stored in a freezer or on dry ice.

\*\* Trip spike carried on dry ice all week.

ND = not detected, <0.030 ug/sample (less than 0.01 ug/m<sup>3</sup> for a 24-hour sample.)

R = Shafter site, BF = Bakersfield site, M = Lamont site and V = Weed Patch site.

$$\text{ppbv} = (\text{ug/m}^3) \times \frac{(8.21 \times 10^{-2} \text{ liter-atm/mole} \cdot \text{K})(298 \text{ K})}{(73.12 \text{ gram/mole})(1 \text{ atm})} = 0.3346 \times (\text{ug/m}^3)$$

TABLE IV. Summary of Ambient MITC Data ( $\mu\text{g}/\text{m}^3$ )

Site	Number of Samples	Number above MDL	Maximum Value	Second Max.	Avg. *
R	8	4	2.2	0.70	0.67
BF	8	8	6.0	5.8	2.1
M	8	8	17.	10.	5.9
V	8	8	18.	12.	8.4

\* of samples above the detection limit.

Minimum detection limit =  $0.030 \mu\text{g}/\text{sample}$  ( $0.01 \mu\text{g}/\text{m}^3$  for a 24-hour sample).

R = Shafter site, BF = Bakersfield site, M = Lamont site and V = Weed Patch site.

Figure I. MITC Monitoring Area

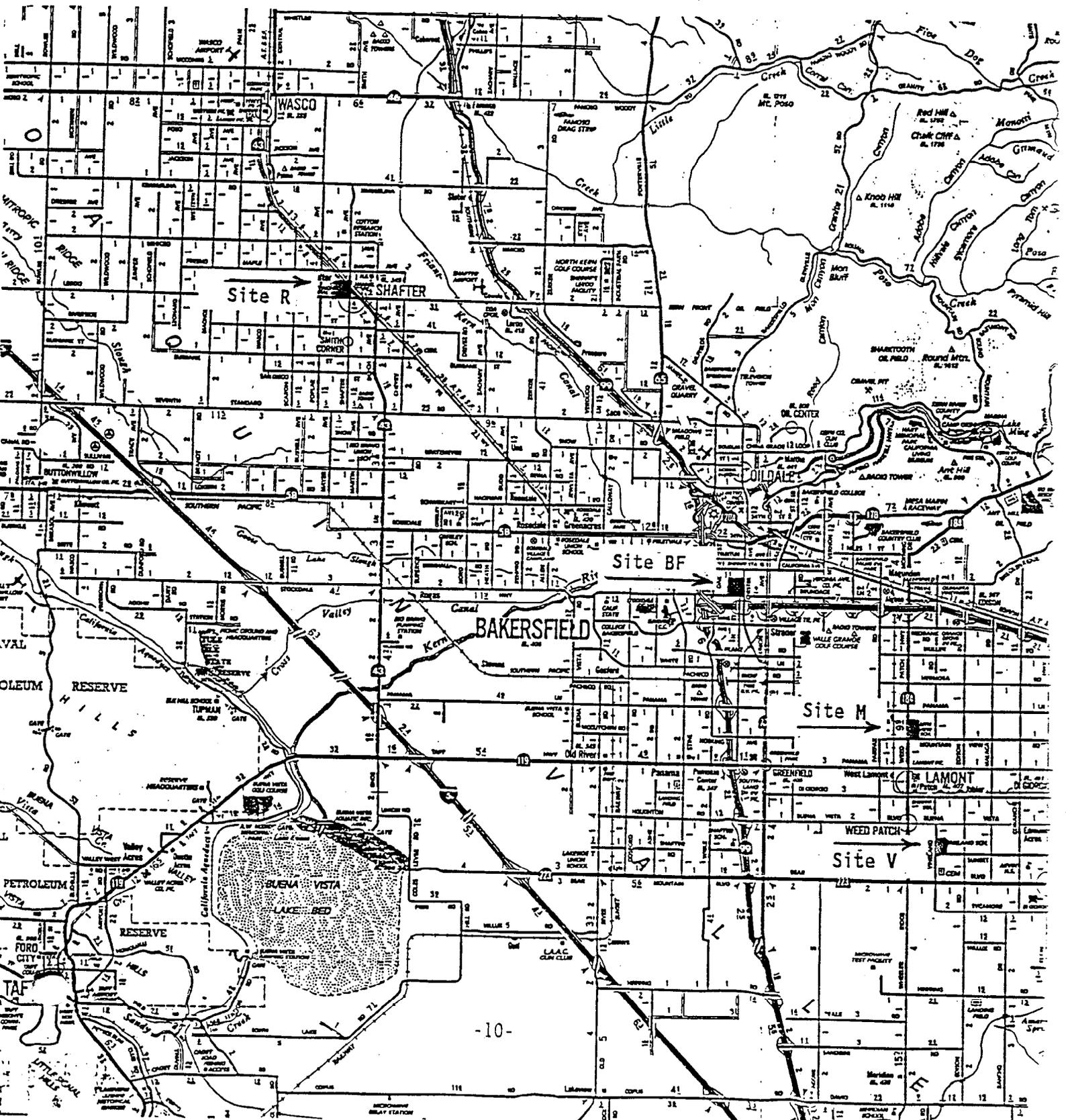


Figure II. Monitoring Apparatus

