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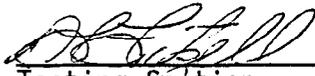
AMBIENT AIR MONITORING FOR MITC IN KERN COUNTY DURING SUMMER 1993
AFTER A GROUND INJECTION APPLICATION OF METAM SODIUM TO A FIELD

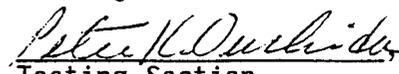
Engineering Evaluation Branch
Monitoring and Laboratory Division

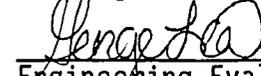
Test Report No. C92-070B

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Ambient Air Monitoring for MITC in Kern County During Summer 1993
after a Ground Injection Application of Metam Sodium to a Field

This report presents the results of ambient air monitoring after a ground injection application of metam sodium at a selected field in Kern County. The effects of the metam sodium application 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. The concentrations determined ranged from 1.2 ug/m³ (0.40 ppbv) to 880 ug/m³ (290 ppbv). The results are based on samples collected by the Air Resources Board Engineering Evaluation Branch staff and analyzed by the staff of the Environmental Health Laboratory Branch, Department of Health Services. 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. David German of Wilbur-Ellis in Shafter, CA arranged for a suitable field to monitor. 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 (EHLB), Department of Health Services. Confirmation of selected samples was completed using GC/MS by EHLB staff.

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After a Ground Injection Application of Metam Sodium to a Field

I. INTRODUCTION

The Air Resources Board (ARB) Engineering Evaluation Branch (EEB) conducted a three-day source impacted ambient monitoring program for an application of metam sodium in Kern County during the summer of 1993. 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 effects of the metam sodium application 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.

The purpose of this monitoring program was to determine MITC concentrations when metam sodium is injected at a high rate into the soil under warm air and warm soil conditions. This monitoring was conducted in order to compare results with two other MITC studies. The first, presented in the report, "Ambient Air monitoring in Contra Costa County during March 1993 after an Application of Metam Sodium to a Field" represents a "best case" ground injection application under cool air and soil conditions. The second study, just completed in August 1993, represents a "worst case" application under warm air and soil conditions, as well as the application being conducted by introducing the metam sodium into sprinkler irrigation water rather than injection into the soil. This sampling of a sprinkler irrigation application was conducted by DPR staff and analyzed by staff of the California Department of Food and Agriculture Laboratory in Sacramento.

Monitoring for carbon disulfide did not occur in this study because the detection limits were not low enough to measure possible emissions from a soil injection application. However, samples for carbon disulfide analysis were taken during the DPR study.

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/m³ (LC₁₀₀, rat 30-minute exposure) to 1900 mg/m³ (LC₅₀, 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/m³ 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/m³). Studies are underway to refine the odor threshold and eye irritation levels for humans.

III. SAMPLING LOCATIONS

A field of about 85 acres was selected (FIGURE I) by David German of Wilbur-Ellis and approved by ARB staff to use for application monitoring. Four samplers were set up (see FIGURE II): one on the east perimeter at a distance of about 40 yards from the field (because of the garden), one about 20 yards from the southern perimeter and one about 20 yards from the western perimeter. Because of the irregular shape of the field and because the metam sodium tank was parked on the northern perimeter, the fourth sampler was placed about 20 yards from the northeastern "corner" of the field.

The application was by tractor and took about three days. Application occurred only during daylight hours. It was applied at a rate of 150 gal/acre. This included 50 gal/acre of Soil Prep (containing 3.1 pounds of metam sodium per gal), 45 gal/acre of 10-34-0 Liquid (fertilizer) and 1.75 gal/acre of zinc chelate 9% liquid (fertilizer) with the remaining volume (up to the 150 gal/acre) made up with water. The application was set for a depth of 10 to 12 inches in soil that would be characterized as sandy loam. Following the application, no soil sealing was used to mitigate possible air emissions. The PCA recommendation is included as APPENDIX IV.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through charcoal tubes (APPENDIX I). 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 II. Duplicate samples were obtained from all sites, but not all duplicates were analyzed. The additional duplicates were archived and not analyzed unless a difficulty in the analysis required it. The application took much longer than most monitored by EEB staff and occurred only during daylight hours. For these reasons, the sampling schedule outlined in the QA Plan (APPENDIX II) was not followed. Sample tubes were changed before application began in the morning, once during the application period and after application ended for the day.

Each sample train consisted of an charcoal tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a 12VDC battery-powered vacuum pump. A diagram of the sampling train is shown in FIGURE III. 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 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 1.88 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 three weeks of collection, except for sample #5W. This sample was inadvertently overlooked and not analyzed until ten weeks after it was collected. It was stored in the freezer during this period. Confirmation was performed on the already extracted samples by Environmental Health Laboratory Branch, Department of Health Services staff using gas chromatography/mass spectroscopy (GC/MS) (TABLE I).

The Jerome analyzer is a hand held instrument that determines levels of hydrogen sulfide based on the reaction of that compound with a gold film surface. The change of electrical conductivity across the gold film due to this reaction is proportional to the hydrogen sulfide concentration. The lowest detectable level is 3 parts per billion by volume (ppbv).

VI. RESULTS

The monitoring results are shown in TABLE II. A summary of the on-site meteorological data is presented in TABLE III. The laboratory data from EHLB and CDFA is presented in APPENDIX V. Additional detailed meteorological data from the California Irrigation Management Information System (CIMIS) station, located in Lamont, is presented in APPENDIX VI. A summary of the monitoring and meteorological data is presented in TABLE IV. None of the results presented in this report have been corrected for percentage recovery or calibration data.

After collection of all of the samples, those in series 3 and 4 were accidentally left in the ice chest over the weekend. They were exposed to ambient temperatures of over 100° F for an unknown period of time after the dry ice was gone. The actual concentrations of these samples is probably higher than the reported values because of degradation. All of the others samples were stored in a freezer until delivered to the laboratory. Sample 5W was overlooked and not analyzed for ten weeks. The actual value may also be higher than reported.

The ground application continued throughout the monitoring period. FIGURE IV is an attempt to graphically correlate the sampling

periods and the application pattern. TABLE IV is an attempt to graphically present the meteorological data and the levels of MITC detected at the various sites. As TABLE II shows, 3 significant levels of MITC were found. Values ranged from 1.2 ug/m³ (0.40 ppbv) to 880 ug/m³ (290 ppbv).

At the beginning of the application a Jerome hydrogen sulfide (H₂S) analyzer was used to measure ambient values (calibration data, APPENDIX VII). The results (uncorrected for calibration data, APPENDIX VII) are shown in TABLE V. Downwind of the application (15 to 25 yards), values did not exceed 8 ppb. Measuring the levels directly above the ground (approx. 3 inches) shortly after injection yielded values of about 10 ppb. At the beginning of the application, a pesticide spill resulted from plugged lines on the tractor. Monitoring the air directly over this surface spill, the maximum concentration was 50 ppb.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Analytical Procedure for metam sodium (APPENDIX III).

Most of the procedures outlined in the Quality Assurance Plan (APPENDIX II) were followed. The exception were: the sampling schedule was changed (see SAMPLING METHODOLOGY) and no field spikes were prepared. Confirmation for the levels of selected field samples was completed by other EHLB staff using GC/MS. The results for GC/MS ranged from 89 - 97% of the values determined by EHLB using GC/NPD. In addition, a flow rate audit, a systems audit and an analytical performance audit was performed by the ARB Quality Management and Operations Support Branch (APPENDIX VIII).

Figure I. MITC Application Monitoring Area

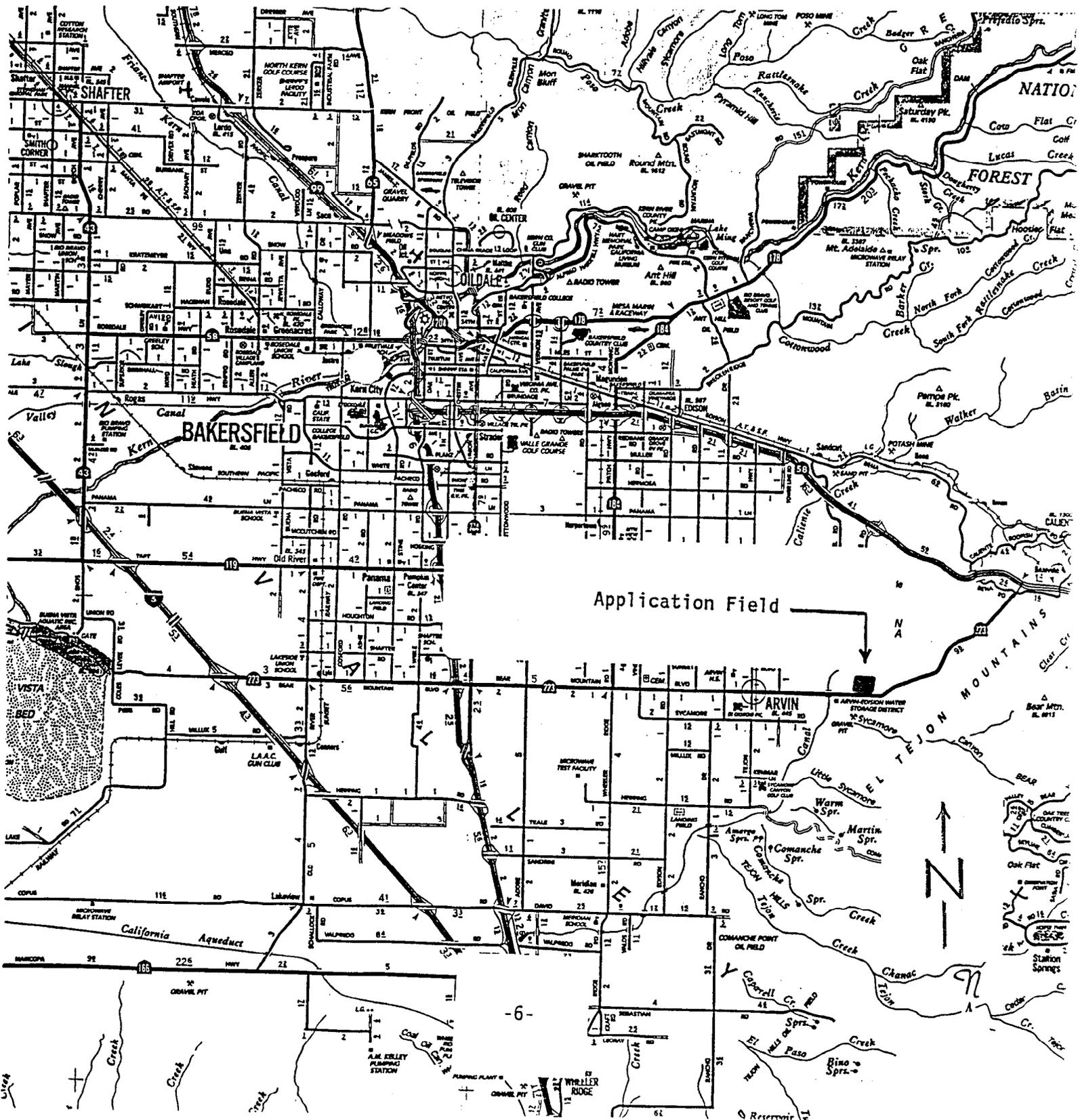


Figure II. MITC Application Monitoring Sites

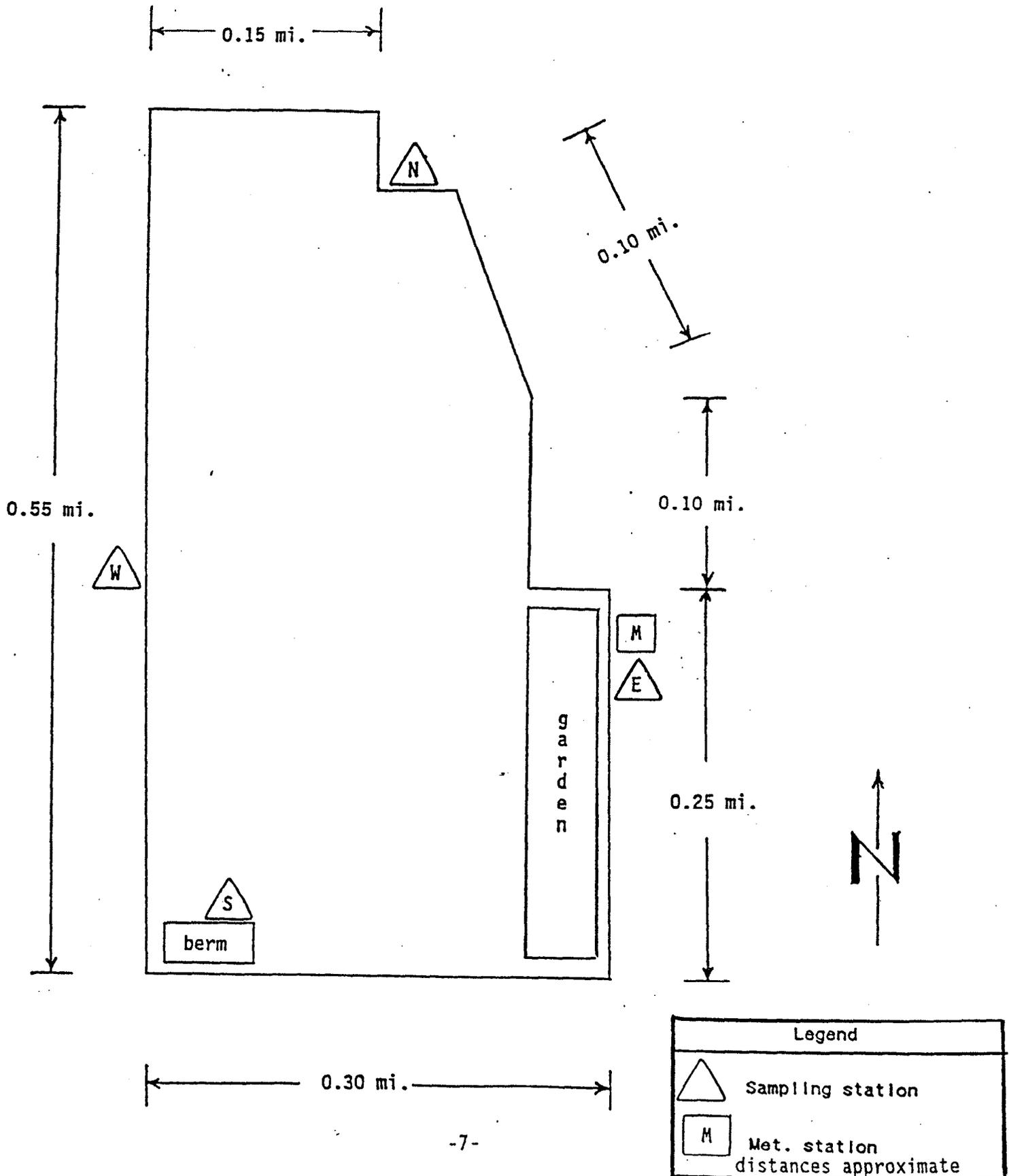


Figure II. MITC Application Monitoring Sites

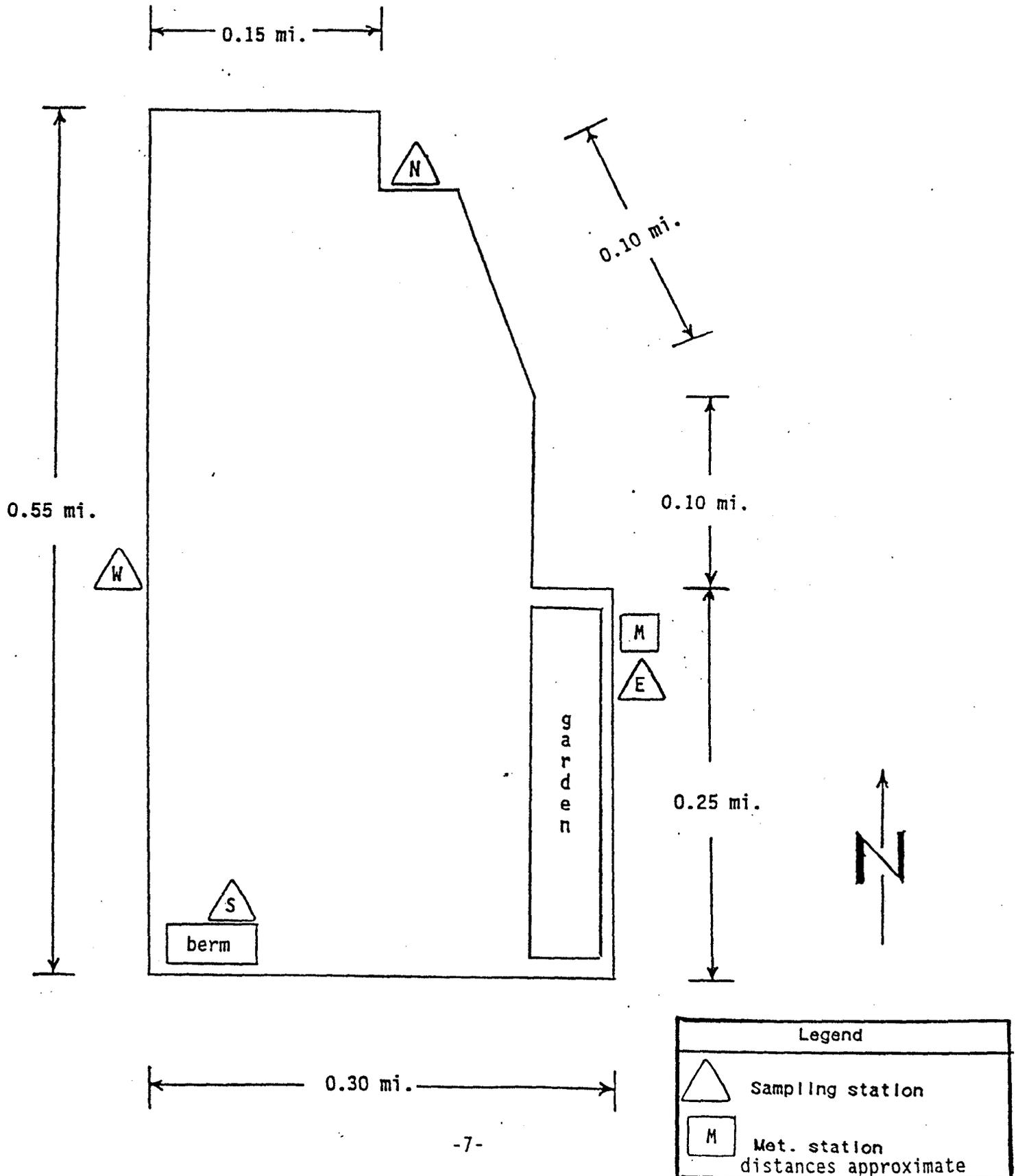


Figure II. MITC Application Monitoring Sites

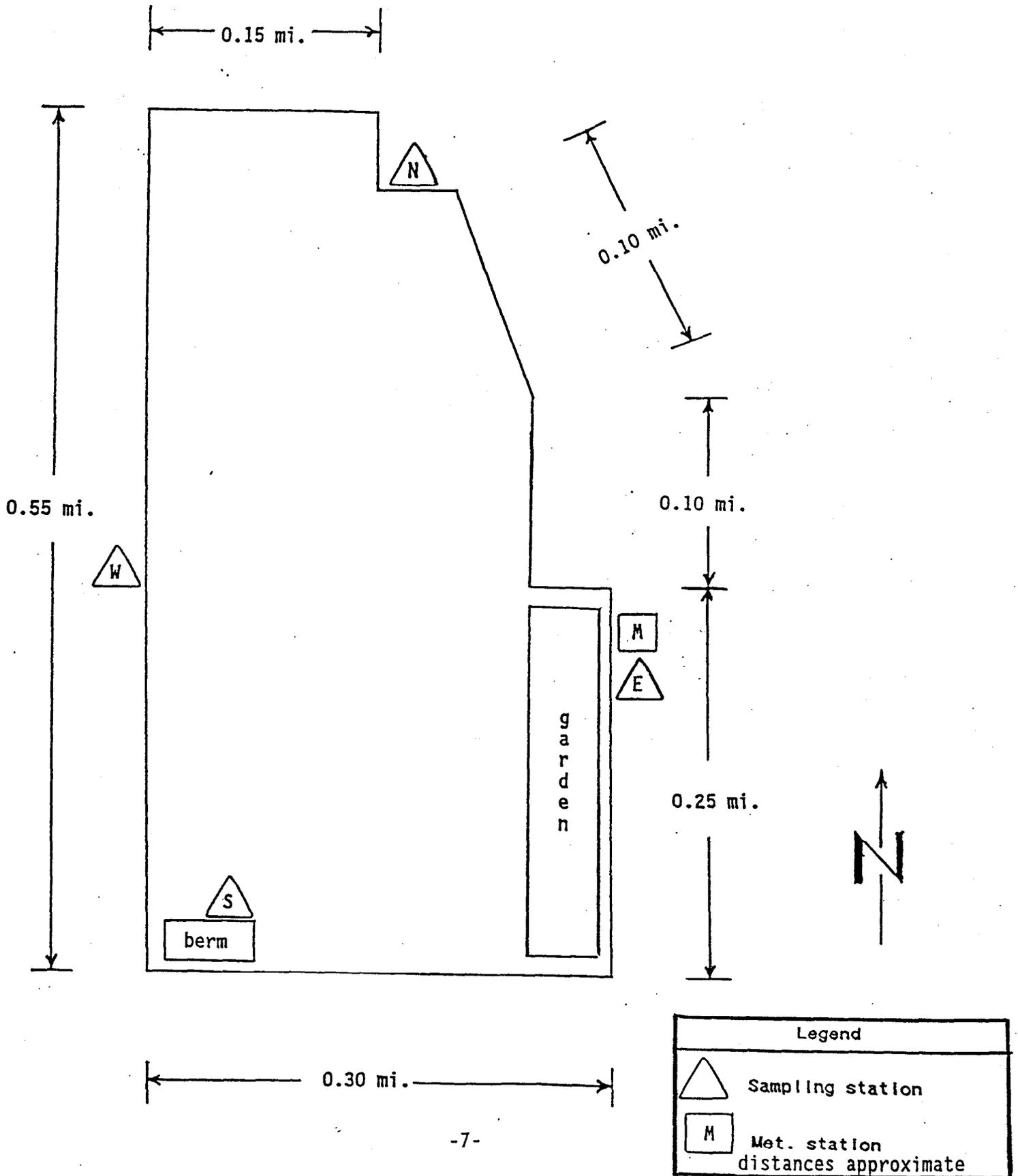


FIGURE III. Monitoring Apparatus

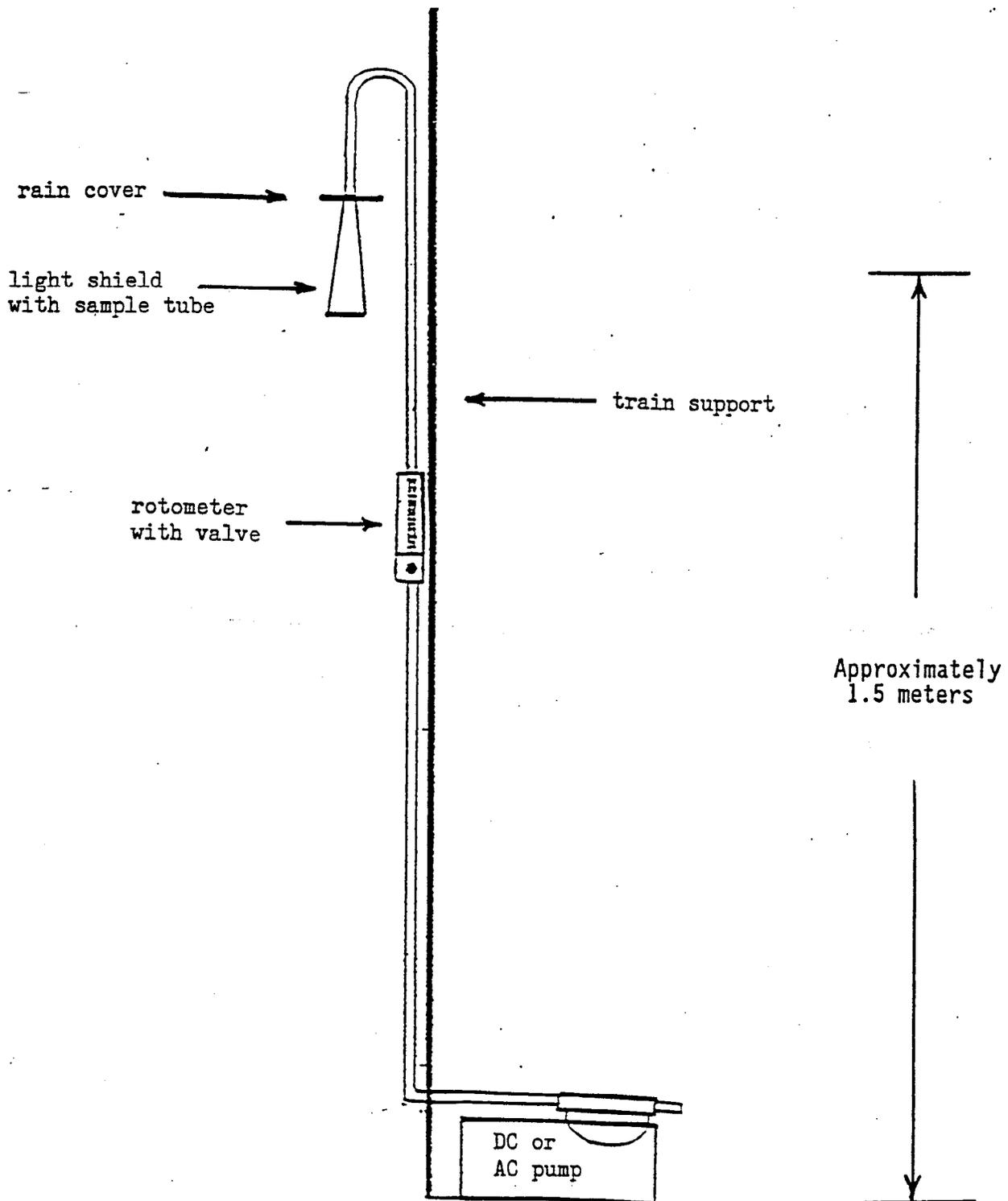
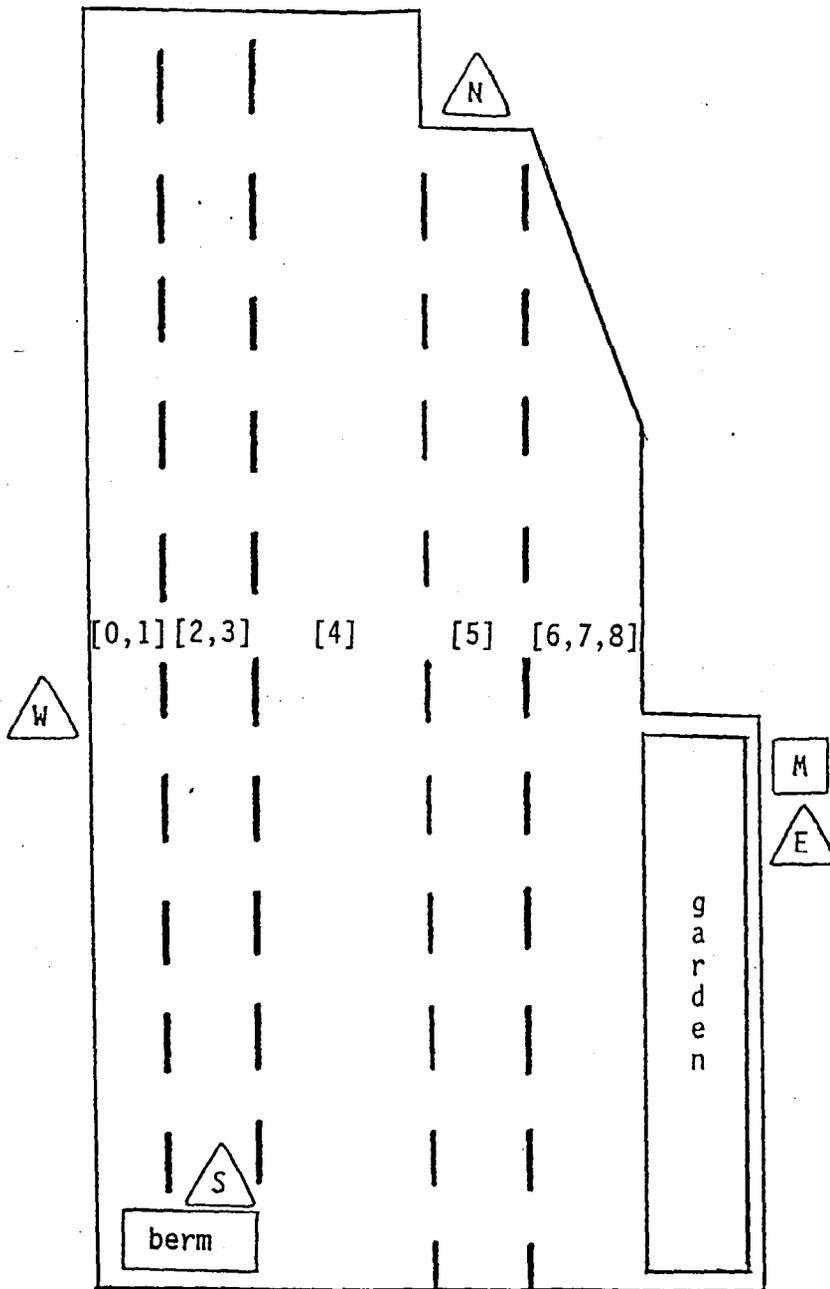


Figure IV. Correlation of Sampling Periods and Application Pattern



Application from west to east.
 Vertical lines divide the field into approximate "areas" applied at different times.
 [] indicates sampling periods completed during the application to the various "areas".



Legend	
	Sampling station
	Met. station

TABLE I. EHLB QA/QC Data

Sample ID	GC/NPD (ug)	GC/MS (ug)
8N	311.	289.
8E	297.	287.
8S	639.	576.
8W	1315.	1176.

TABLE II. MITC Application Monitoring Data

Sample ID	Time (min.)	Volume* (m ³)	Total (ug)	Concentration (ug/m ³) (ppbv)		Collection Time (Approx.)
0W	110	0.21	0.745	3.6	1.2	Background
0N	115	0.22	0.697	3.2	1.1	
0E	115	0.22	0.694	3.2	1.1	7/27/93 (0700-0915)
0S	130	0.24	0.617	2.6	0.87	
1W	365	0.69	1.62	2.3	0.77	Application Begins
1N	370	0.70	1.63	2.3	0.77	
1E	375	0.70	1.02	1.5	0.50	7/27/93 (1215-1830)
1S	385	0.72	4.70	6.5	2.2	
2W	730	1.4	809.	580.	190.	7/27-28/93 (1830-0630)
2N	720	1.4	37.1	26.	8.7	
2E	730	1.4	6.53	4.7	1.6	7/27-28/93 (1830-0630)
2S	725	1.4	36.7	26.	8.7	
3W	315	0.59	71.8	120.	40.	7/28/93 (0630-1200)
3N	315	0.59	2.32	3.9	1.3	
3E	315	0.59	1.48	2.4	0.80	7/28/93 (0630-1200)
3S	315	0.59	15.4	26.	8.7	
3B	BLANK	--	ND	--	--	
4W	345	0.65	0.785	1.2	0.40	7/28/93 (1200-1730)
4N	345	0.65	45.8	70.	23.	
4E	345	0.65	3.76	5.8	1.9	7/28/93 (1200-1730)
4S	345	0.65	17.2	26.	8.7	
5W	785	1.5	303.	200.	67.	7/28-29/93 (1730-0700)
5N	785	1.5	1180.	800.	270.	
5E	790	1.5	153.	100.	33.	7/28-29/93 (1730-0700)
5S	795	1.5	382.	250.	84.	
6W	370	0.70	65.9	94.	31.	7/29/93 (0700-1300)
6N	370	0.70	63.2	90.	30.	
6E	360	0.68	6.14	9.0	3.0	7/29/93 (0700-1300)
6S	360	0.68	5.50	8.1	2.7	
7W	285	0.54	0.653	1.2	0.40	7/29/93 (1300-1800)
7N	290	0.54	27.6	51.	17.	
7E	295	0.56	65.9	120.	40.	7/29/93 (1300-1800)
7S	295	0.56	4.79	8.6	2.9	
8W	785	1.5	1315.	880.	290.	7/29-30/93 (1800-0700)
8N	780	1.5	311.	210.	70.	
8E	775	1.5	297.	200.	67.	7/29-30/93 (1800-0700)
8S	780	1.5	639.	430.	140.	

* All flows at 1.88 liters per minute (see SAMPLING METHODOLOGY).

ND = Not Detected, <0.030 ug/sample (<0.021 ug/m³ for a 12-hour sample).

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

Series 3 and 4 were exposed to high temperatures during storage and the values reported are probably low. Sample 5W was analyzed later than the other samples and may also be low (see RESULTS).

No values corrected for percentage of recovery.

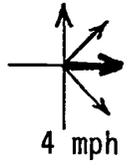
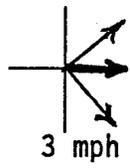
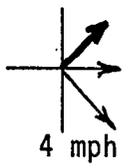
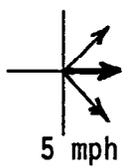
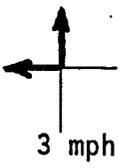
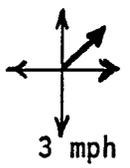
TABLE III. MITC Meteorological Data

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

BOLD indicates predominant wind direction, if any.

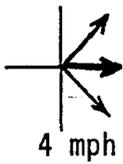
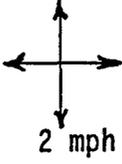
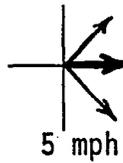
* Indicates direction wind blows from.

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

<p>(0) [W] <u>3.6</u> [N] <u>3.2</u></p>  <p>[E] <u>3.2</u></p> <p>4 mph</p> <p>[S] <u>2.6</u></p>	<p>(3) [W] <u>120.</u> [N] <u>3.9</u></p>  <p>[E] <u>2.4</u></p> <p>3 mph</p> <p>[S] <u>26.</u></p>
<p>(1) [W] <u>2.3</u> [N] <u>2.3</u></p>  <p>[E] <u>1.5</u></p> <p>4 mph</p> <p>[S] <u>6.5</u></p>	<p>(4) [W] <u>1.2</u> [N] <u>70.</u></p>  <p>[E] <u>5.8</u></p> <p>5 mph</p> <p>[S] <u>26.</u></p>
<p>(2) [W] <u>580.</u> [N] <u>26.</u></p>  <p>[E] <u>4.7</u></p> <p>3 mph</p> <p>[S] <u>26.</u></p>	<p>(5) [W] <u>200.</u> [N] <u>800.</u></p>  <p>[E] <u>100.</u></p> <p>3 mph</p> <p>[S] <u>250.</u></p>

() Indicates sampling period. [] Indicates sampling site.
 Arrow indicates direction wind is blowing toward. **Bold** indicates predominant wind direction, if any.
 Samples from periods 3 and 4 were exposed to high temperatures and the actual values are probably are higher. Sample 5W was analyzed late and may also be higher than reported. (see RESULTS)

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

<p>(6) [N] <u>90.</u> [W] <u>94.</u> [E] <u>9.0</u> 4 mph [S] <u>8.1</u></p> 	<p>(8) [N] <u>210.</u> [W] <u>880.</u> [E] <u>200.</u> 2 mph [S] <u>430.</u></p> 
<p>(7) [N] <u>51.</u> [W] <u>1.2</u> [E] <u>120.</u> 5 mph [S] <u>8.6</u></p> 	

() Indicates sampling period. [] Indicates sampling site.
Arrow indicates direction wind is blowing toward. Bold indicates predominant wind direction, if any.

MITC Application, Kern Co.

TABLE V. Jerome Hydrogen Sulfide Readings (PPB)

7/27/93

Site	Time	PPB	Comments
------	------	-----	----------

(Background)

S	0930	1-2 on berm, 1-3 on field (2 1/2 ft.), one excursion to 10	
W	0940	7-16 [0-4 near tanks], 0-2	
N	0950	1-2	
E	0955	1-2	
MITC tank	0950	8-11, [125-154 above open tank]	

(Start Application)

W	1800	1-4 [2 in van]	
N	1805	0-3	
E	1810	1-6	
S	1815	0-1	
N (near start of application)	1225	0-5	

7/28/93

N	0630	0-1	
E	0640	0-2	
S	0645	0-2	
W	0650	6-9	
near tank	0700	0-4	
W	1145	0-1	
N	1150	1-2	
E	1200	0-1	
S	1205	0-2	
		0-2	3 ft. above appl. (approx. 30 min. after appl.)
		30-50	3 in. above spill
		8-12	3 in. above appl. (approx. 15 min. after appl.)
W	1730	1-2	
N	1735	0-2	
E	1740	0-1	
S	1745	1-3	

Values not corrected for calibration data (APPENDIX VII).