State of California

AIR RESOURCES BOARD

MOLINATE APPLICATION MONITORING REPORT

Molinate Ambient Air Monitoring in Colusa County, May 1992

Engineering Evaluation Branch

Monitoring and Laboratory Division

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Abstract

This report presents the results of source impacted ambient monitoring for molinate after an aerial application at a selected rice field in Colusa County. Additional ambient air monitoring was conducted in the two nearby communities of Williams and Maxwell. Molinate was found above the detection level in both the application and community monitoring. The results are based on samples collected by the Air Resources Board (ARB) staff and analyzed by the staff of the Department of Environmental Toxicology (DET), University of California, Davis. Based on the quality control measures employed by the Air Resources Board and DET staff the results are believed to be accurate within the limits of the methods.

Acknowledgments

Lorraine Caldwell of Caldwell Flying Service greatly helped 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 Mike McChesney of the Department of Environmental Toxicology, UC Davis.

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I. INTRODUCTION

At the request of the Cal/EPA Office of Environmental Health Hazard Assessment (OEHHA), the 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-day source impacted ambient monitoring program for molinate (APPENDIX I). This monitoring was conducted in Colusa County during May, 1992, representing the place and the time where the peak use of molinate occurs. Other fields in the vicinity were applied during the monitoring period. The monitoring program consisted of determining molinate concentrations in populated areas and in the vicinity of where one application of molinate occurred.

II. PESTICIDE DESCRIPTION

Molinate (molecular weight 173.3 g/mole) is a selective herbicide used to control water grass in rice fields. The herbicide is applied as granules from the air. Its solubility in water is 880 milligrams/liter (mg/l). It is miscible with acetone, ethanol and xylene. The vapor pressure of molinate is 4.1×10^{-4} kilopascal (kPa) at 20^{0}C.

Molinate is not regulated as a restricted use material under section 6400, Title 3 of the California Code of Regulations. Ordram 10-G, a 10% granular formulation of molinate, has an oral LD_{50} of greater than 5,000 milligram/kilogram (mg/kg) for rats and a dermal LD_{50} of 3,536 mg/kg for rabbits (Farm Chemicals Handbook, 1990).

III. SAMPLING METHODOLOGY

The sampling method is based on passing measured quantities of ambient air through a tube that has two XAD Sections (APPENDIX II). The tube had a dimension of 8 mm x 110 mm, and has with 400 mg and 200 mg of XAD in the primary and secondary sections (SKC catalog #226-30-06). Any molinate present in the sampled ambient air is captured by the XAD-2 adsorbent contained in the tubes. After completing the field sampling program, the tubes were transported in an iced container to the University of California, Davis, Department of Environmental Toxicology (DET) for analysis.

Each sample train consisted of an XAD-2 tube with tube cover, Teflon fittings and tubing, rain shield, rotometer, train support, and either a 12VDC or 115VAC vacuum pump. Battery-powered pumps were used where line power was not available. A diagram of the sampling train is shown in FIGURE I. This configuration was used for both application

monitoring and ambient monitoring in populated areas. 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) for the application site DC-powered monitors and 4.5 lpm for the populated area AC-powered ambient monitors. A leak check was performed by blocking off the sample inlet. The sampling train was 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 or 4.5 lpm and was recorded (if different from the planned setting) along with date, time, and site location. Calibration by bubble meter prior to use in the field indicated that an average flow rate of 1.90 lpm was actually achieved when the rotometers were set to 2.0 lpm (battery powered) and 3.74 lpm when the rotometers were set at 4.5 lpm (AC powered). These average values were used to calculate sample volumes for all samples. If a change of flow rate occurred, the average of the starting and final flow rate was used. Both of these flow rates would be determined by bubble meter calibration.

At the end of each sampling period the final indicated flow rate (if different than the set value), the stop date and time were recorded. The XAD-2 tubes were then removed from the sample train, end caps installed on both ends, and an identification label affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest until the tubes were delivered to the laboratory for analysis.

IV. SAMPLING LOCATIONS

The pesticide monitoring area including the ambient monitoring sites as well as the application sites, is shown in FIGURE II. Battery-powered sampling trains designed to operate continuously were set up at four sampling sites (N2,N1,S1 and S2) near the application field (FIGURE III) and 115VAC line-powered sampling trains were set up at fire stations in Williams and Maxwell for the ambient monitoring.

The application site was a rice field of approximately 99 acres (FIGURE III) selected by Lorraine Caldwell of Caldwell Flying Service and approved by ARB staff. The molinate was applied in the formulation, Ordram 10-G, as granules from the air at a rate of fifty pounds per acre. Ordram 10-G consists of 10% molinate, the active ingredient. The application took approximately an hour and a half. The prevailing wind in the area is from the north. Four samplers were set up; 1) approximately 10 yards north of the field, 2) approximately 25 yards south of the field, 3) approximately one quarter mile south of the field and 4) approximately one quarter mile northwest of the field. This latter site was chosen because no access was available directly

north of the field. A meteorological station was set up near the downwind sampler (S1) nearest the field (FIGURE III).

The sample tubes in the application monitors were changed at varying intervals (APPENDIX II) for the first 24 hours. Thereafter the two samplers nearest the field (N1 and S1) were changed every 12 hours and the two farthest from the field (N2 and S2) were changed every 24 hours. The tubes in the ambient monitors (Williams and Maxwell) were changed every 24 hours.

V. ANALYTICAL METHODOLOGY

The XAD-2 tubes recovered from each sampler were analyzed by UC Davis DET staff. The XAD-2 in each sample tube was extracted with ethyl acetate followed by gas chromatography (GC) separation on a DB-5 column and quantitation using a Nitrogen/Phosphorous Detector (NPD) (APPENDIX II).

VI. RESULTS

The analytical results for the application monitoring are shown in TABLE I. The results of the ambient air monitoring in Williams and Maxwell are shown in TABLE II. The meteorological data is presented in TABLE III. A summary of the application results along with meteorological data is shown in TABLE IV. Some of the results in TABLE I, II and IV are the average of duplicate samples. For a comparison of these duplicate samples as well as the triplicate analysis for each sample, see APPENDIX III. TABLE V summarizes the quality assurance data involved for both the application and ambient analytical work.

The highest levels adjacent to the field occurred on the afternoon (sampling period 4) following the application (22.61 ug/m^3). The values decreased from this time, but significant levels (6.27 ug/m^3) were still detected on the last day of monitoring.

Low, but detectable levels (0.16 to 1.17 ug/m^3) were measured throughout the ambient monitoring in Williams and Maxwell.

VII. QUALITY ASSURANCE

Reproducibility, linearity, minimum detection limit, collection and extraction efficiency, breakthrough and storage stability are described in "Airborne Residues Resulting from Use of Methyl Parathion, Molinate and Thiobencarb on Rice in the Sacramento Valley, California" (APPENDIX IV). However, the sampling apparatus used in this earlier study was significantly different than that used this time. Financial limitations prevented repeating all of this quality assurance work. Although QA spike data (APPENDIX V) resolve collection and extraction efficiency, they do not answer the question of breakthrough above the level used (0.97 ug/tube). Therefore, all values above this level must be considered a minimum because of the possibility of breakthrough.

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX V) were followed. The ARB Quality Management and Operations Support Branch (QMOSB) performed a Quality Assurance audit (see APPENDIX VI for full report). This included a laboratory audit in which five sample tubes containing various amounts of molinate were submitted to DET for analysis. A summary of the laboratory audit results are shown in TABLE V. The difference between the assigned and the reported values ranged from -10.3 to 0%.

TABLE I. MOLINATE APPLICATION MONITORING DATA

Sample ID	Sample Period[1]	Time (min.)	Volume (m^3)	Mass[2,3] (ug)	Concentration (ug/m^3)	Date Time (Approx.)
1N1		65	0.124	<0.06	--	
1S1	1(D)	70	0.133	0.22	1.65	(Background)
1N2		sample not taken				5/18/92
1S2		60	0.114	<0.06[2]	--	0830-1000
2N1		120	0.228	2.09[2]	9.17	
2S1	2(D)	125	0.238	0.59[2]	2.48	(Application)
2N2		95	0.181	<0.06[2]	--	5/18/92
2S2		130	0.247	0.11[2]	0.45	1100-1330
3N1		115	0.219	2.48	11.32	
3S1	3(D)	115	0.219	0.80	0.37	
3N2		120	0.228	<0.06	--	5/18/92
3S2		115	0.219	0.06	0.27	1330-1530
3B		BLANK		<0.06	--	
4N1		155	0.295	6.67	22.61	
4S1	4(D)	155	0.295	1.17	3.97	
4N2		155	0.295	<0.06	--	5/18/92
4S2		155	0.295	<0.06	--	1530-1800
5N1		740	1.406	14.26	10.14	
5S1	5(N)	740	1.406	3.73	2.65	
5N2		745	1.416	0.84	0.59	5/18-19/92
5S2		740	1.406	0.80	0.57	1800-0600
6N1		695	1.321	11.39	8.62	5/19/92
6S1	6D	700	1.330	2.69	2.02	0600-1800
6N2		1435	2.727	0.81	0.30	5/19-20/92
6S2	6(D+N)	1440	2.736	2.34	0.86	0600-0600
7N1		745	1.416	3.43	2.42	5/19-20/92
7S1	7N	740	1.406	4.80	3.41	1800-0600
8N1		700	1.330	0.46	0.35	5/20/92
8S1	8D	700	1.330	9.10	6.77	0600-1800
8N2		1440	2.736	1.24	0.45	5/20-21/92
8S2	8(D+N)	1455	2.765	7.25	2.62	0600-0600
9N1		750	1.425	2.14	1.50	5/20-21/92
9S1	9N	760	1.444	9.25	6.41	1800-0600
10N1		690	1.311	0.16	0.12	5/21/92
10S1	10D	685	1.302	7.78	5.98	0600-1800
10N2		1615	3.069	4.05	1.32	5/21-22/92
10S2	10(D+N)	1615	3.069	9.94[2]	3.24	0630-0900
11N1		920	1.748	5.74[2]	3.28	5/21-22/92
11S1	11N	925	1.758	11.02	6.27	1800-0900

[1] D = daytime (approx. 0600-1800), N = nighttime (approx. 1800-0600).

[2] Average of duplicate samples.

[3] ND = not detected, <0.06 ug/sample.

TABLE II. MOLINATE AMBIENT AIR MONITORING DATA

Site	Volume Sampled (m^3)	Sample Time (min.)	Mass Detected (ug)	Concentration (ug/m^3)	Date
Williams	4.81	1285	1.94	0.40	5/20-21/92
Williams	6.02	1610	0.94	0.16	5/21-22/92
Williams	5.33	1425	2.54*	0.48	5/26-27/92
Williams	5.39	1440	2.70	0.50	5/27-28/92
Williams	(5.72)	1530	1.47	(0.26)	5/28-29/92
Maxwell	4.38	1170	1.74	0.40	5/20-21/92
Maxwell	6.02	1610	5.42*	0.90	5/21-22/92
Maxwell	5.35	1430	6.25	1.17	5/22-23/92
Maxwell	5.39	1440	2.76	0.51	5/27-28/92
Maxwell	5.55	1485	3.54	0.64	5/28-29/92

*Average of duplicate samples.

( ) indicates estimated volume based on estimated end time.

Flow rate for all samples = 3.74 liters per minute.

TABLE III. MOLINATE METEOROLOGICAL DATA

Sampling Period	Wind Direction*	Average Wind Speed (mph)
1D	S/**SW**	3
2D	S/**SE**	5
3D	**S**/SW	8
4D	**SW**/W	12
5N	**W**/SW	7
6D	S/SW/W	8
6(D+N)	S/SW/W/NW/NE	7
7N	**NW**/W/NE	6
8D	**NE**/NW	9
8(D+N)	N/NE/NW	6
9N	N/NE/NW	4
10D	NE	10
10(D+N)	NW/NE/E/W	6
11N	NW/NE/E/W	2

BOLD indicates predominate wind direction, if any.
Direction wind is blowing from.

TABLE IV. SUMMARY OF MOLINATE APPLICATION DATA (ug/m^3)

[N2]	--	0.59	--	1.32
[N1]	ND	10.14	0.35	--
	(1D) 3 mph 	(5N) 7 mph 	(8D) 9 mph 	(10D+N) 6 mph 
[S1]	1.65	2.65	6.77	--
[S2]	ND	0.57	--	3.24
[N2]	ND	--	0.45	--
[N1]	9.17	8.62	--	3.28
	(2D) 5 mph 	(6D) 8 mph 	(8D+N) 6 mph 	(11N) 2 mph 
[S1]	2.48	2.02	--	6.27
[S2]	0.45	--	2.62	--
[N2]	ND	0.30	--	
[N1]	11.32	--	1.50	
	(3D) 8 mph 	(6D+N) 7 mph 	(9N) 4 mph 	
[S1]	0.37	--	6.41	
[S2]	0.27	0.86	--	
[N2]	ND	--	--	
[N1]	22.61	2.42	0.12	
	(4D) 12 mph 	(7N) 6 mph 	(10D) 10 mph 	
[S1]	3.97	3.41	5.98	
[S2]	ND	--	--	

( ) indicates sampling period, D = daytime (approx. 0600-1800), N = nighttime (approx. 1800-0600).

ND = not detected, <0.06 ug/sample. -- indicates sample not collected during that time period.

[ ] indicates sampling site.

Arrow indicates direction wind is blowing toward.

TABLE V. MOLINATE QUALITY ASSURANCE DATA

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
MO-1	0.49	0.49	0
MO-2	0.29	0.26	-10.3
MO-3	0	ND	N/A
MO-4	0.97	0.96	-1.0
MO-5	0.29	0.28	-3.4

FIGURE 1. PESTICIDE MONITORING APPARATUS

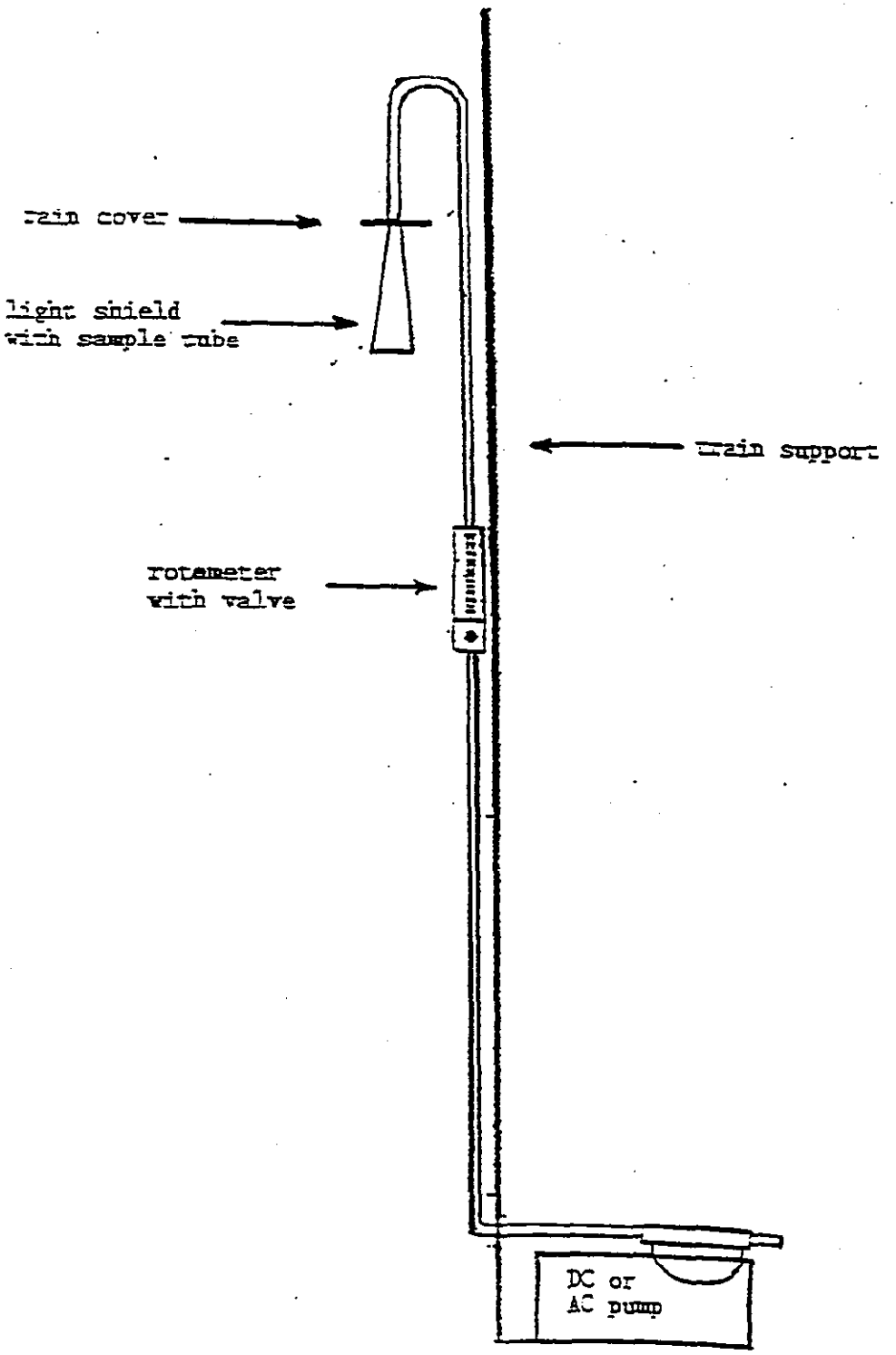

FIGURE 11. PESTICIDE MONITORING AREA

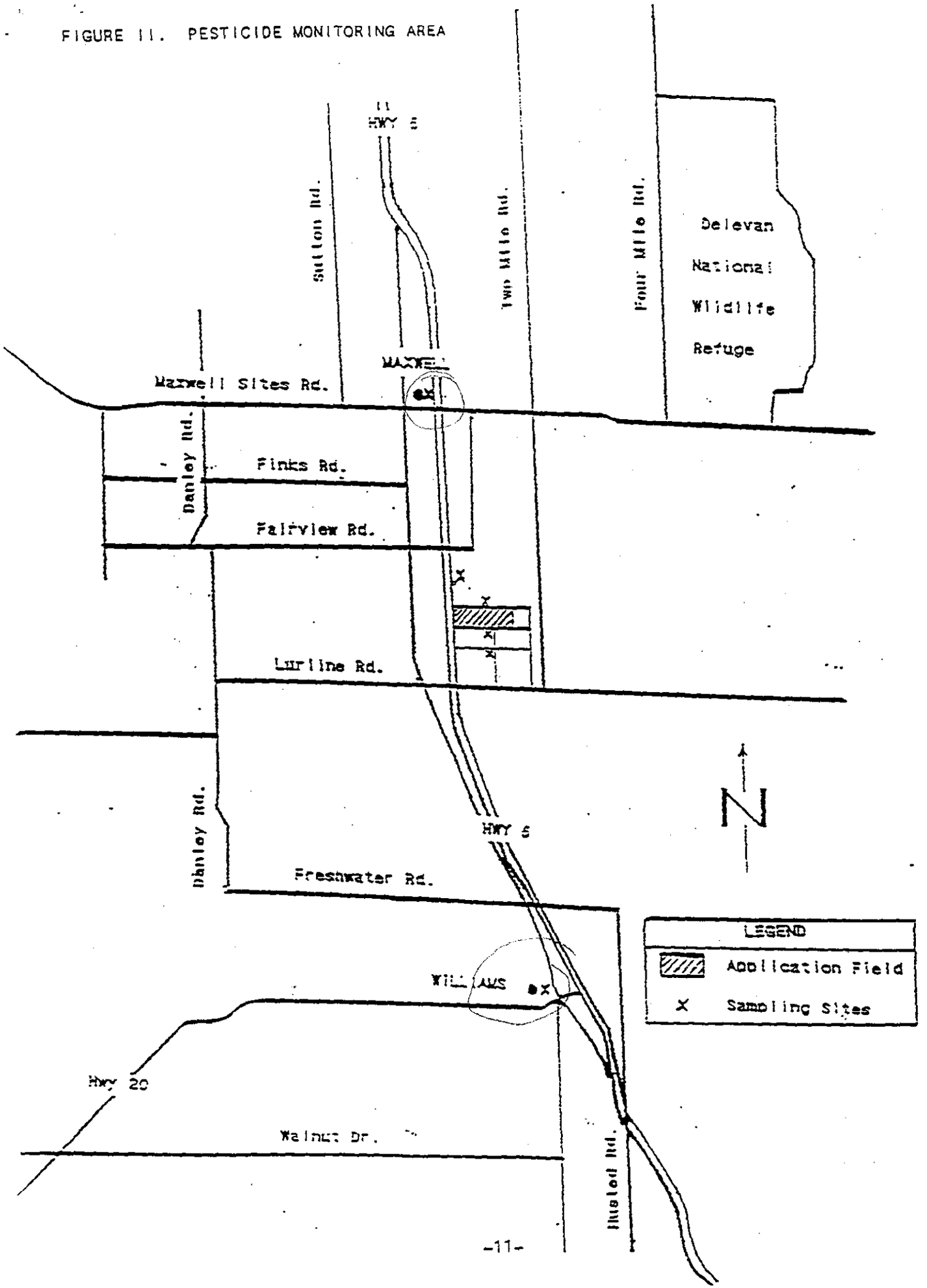

FIGURE III. PESTICIDE MONITORING SITES