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Report on Pesticide Air Monitoring Alongside a Canal Application of Acrolein In Kern County during July 2007

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Monitoring Report Approval

Report Title: Report on Pesticide Air Monitoring Alongside a Canal Application of Acrolein in Kern County during July 2007

Project Lead: Steve Rider, Air Pollution Specialist

Approval: The following monitoring report has been reviewed and approved by the Monitoring and Laboratory Division.

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Executive Summary

Report on Pesticide Air Monitoring Alongside a Canal Application of Acrolein In Kern County during July 2007

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) conducted air monitoring for the pesticide Acrolein during the application of Magnacide H Herbicide (common trade name: Acrolein) in Kern County on July 24th and 25th, 2007. This herbicide is primarily used to control weeds and algae growing in canals or ponds. Sampling was performed alongside a canal within the 0 - 1 mile section and also within the 3.5 - 4.5 mile section. The application rate was 0.17 gallons per cubic feet/second over three hours.

A total of twenty, 4.25-hour integrated air samples, along with five quality control (QC) samples were collected by staff of the Air Quality Surveillance Branch. Each monitored section of the canal included four pairs of samplers placed equidistant from the water's edge every 0.33 miles along the canal. Each section also contained a collocated sampler adjacent to the first east site. In addition, section 0 – 1 had one each additional sampler installed sixty five feet from the 0.3 mile sites. ARB used evacuated Summa canisters equipped with Siltek coated flow controllers to collect the samples. The collected air samples were analyzed using gas chromatography/mass spectrometry by ARB's Northern Laboratory Branch in Sacramento.

- Reported Acrolein results from twenty samples indicated ambient concentrations ranging from 1.0 ppb during background sampling to a maximum of 7.3 ppb occurring 0.3 miles "downstream" from the application point on the west side of the canal, and 65 feet from the edge of the canal.

- The second highest concentration of 6.8 ppb was measured at the 3.5W site. This was the highest concentration measured close to the canal.

Quality control field samples included 2 collocated pairs, 1 field spike, 1 trip spike and 1 trip blank. The Relative Percent Difference (RPD) of the collocated pairs for Acrolein were +25.6% and -25.6%. The field spike recovery was 102%. The trip spike recovery was 101%. The trip blank result was less than the Limit of Detection (LOD) of <0.3 ppb.

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1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR) (January 29, 2007 Memorandum, Warmerdam to Witherspoon), the Air Resources Board (ARB) staff conducted air monitoring for acrolein which is the main ingredient in the application of the herbicide Magnacide H. Acrolein is primarily used in canals or ponds for the control of weeds and algae.

Twenty canister samples and five quality control (QC) samples were collected at eighteen sites alongside a Canal in northwestern Kern County. Two sites included a collocated sampler within two meters of the primary sampler. Monitoring was performed during the period of July 24 -25, 2007. This monitoring was performed under the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB, "…to document the level of airborne emissions…of pesticides that may be determined to pose a present or potential hazard...", when requested by the DPR. Application information is listed in Table 1 (Application Information) and application sampling periods are listed in Table 2 (Application Sampling Periods) on page 8.

2.0 Deviations From Protocol

According to the Sampling Protocol (Appendix A), ARB was to monitor the 4.0 - 5.0 mile section of the canal. However, this would place the last set of canisters within 0.1 miles of Highway 46. Because vehicle exhaust is also a source of acrolein emissions, the section of the canal monitored was moved back 0.5 miles to cover the 3.5 - 4.5 mile section.

According to the sample protocol, sampling was to begin 5-minutes prior to the start of the acrolein application. Upon arrival at the injection point at 0517 hours, after setup of the 3.5 – 4.5 mile section, ARB discovered that the application had started at 0510 hours without any samplers being started. At ARB's request, the applicator stopped the application at 0520 hours. The application was restarted at 0530 hours along with the 0E and 0W samplers.

The sampling protocol states that downstream samplers were to start upon the notification of the arrival of the acrolein plume from water samples obtained two hundred feet upstream from site 3.5E. Baker Petrolite staff was not available to analyze samples for the plumes arrival. Thus, ARB staff started the first 3.5 – 4.5 mile section's samplers at 0745 hours based on the previously measured flow rate of the canal's water of 1.5 mph. Baker Petrolite staff was able to sample and analyze canal water at 0758 hours. The analysis showed a weak presence of Acrolein.

3.0 Sampling Sites

The site nomenclature for this study was generated by identifying each site based upon the mileage point along the canal starting at the application point and proceeding downstream. Since most of the canal generally ran north and south, each side was designated as east (E) or west (W).

Canister samplers were placed every 0.33 miles starting at the gate where the injected acrolein entered the canal to one mile downstream on the 0 - 1 mile section. Due to the variability in the width and condition of the roads on either side of the canal, the east and west side samplers were placed between twenty one and twenty nine feet from the water's edge of the canal. In all cases, east and west side samplers were placed equidistant from the water's edge. Two additional samplers were placed sixty five feet away from the 0.3E and 0.3W samplers, indicated as –L (lateral) samplers. A collocated sampler was located at the 0E site which was the projected downwind site for this area during the summer months.

Further downstream from the acrolein application site, samplers were placed every 0.33 miles starting at the 3.5-mile point from the entry gate to the 4.5-mile point downstream. Due to the variability in the width and condition of the roads on either side of the canal, the east and west side samplers were placed between eighteen and twenty three feet from the water's edge of the canal. In all cases, east and west side samplers were placed equidistant from the water's edge. A collocated sampler was located at the 3.5E site.

Samplers located on the east side of the canal were used as the reference measurement side for each 0.33-mile point. Due to the curvature of the canal, samplers located on the west side of the canal were not spaced exactly 0.33 miles from each other. Exact placement and details are listed on page 9 and 10 in Table 3: Sampler Waypoints, and are displayed on the topographical maps and aerial photos located on pages 3-7, Figures 1-7. Also see Appendix B for site photographs and the pesticide label.

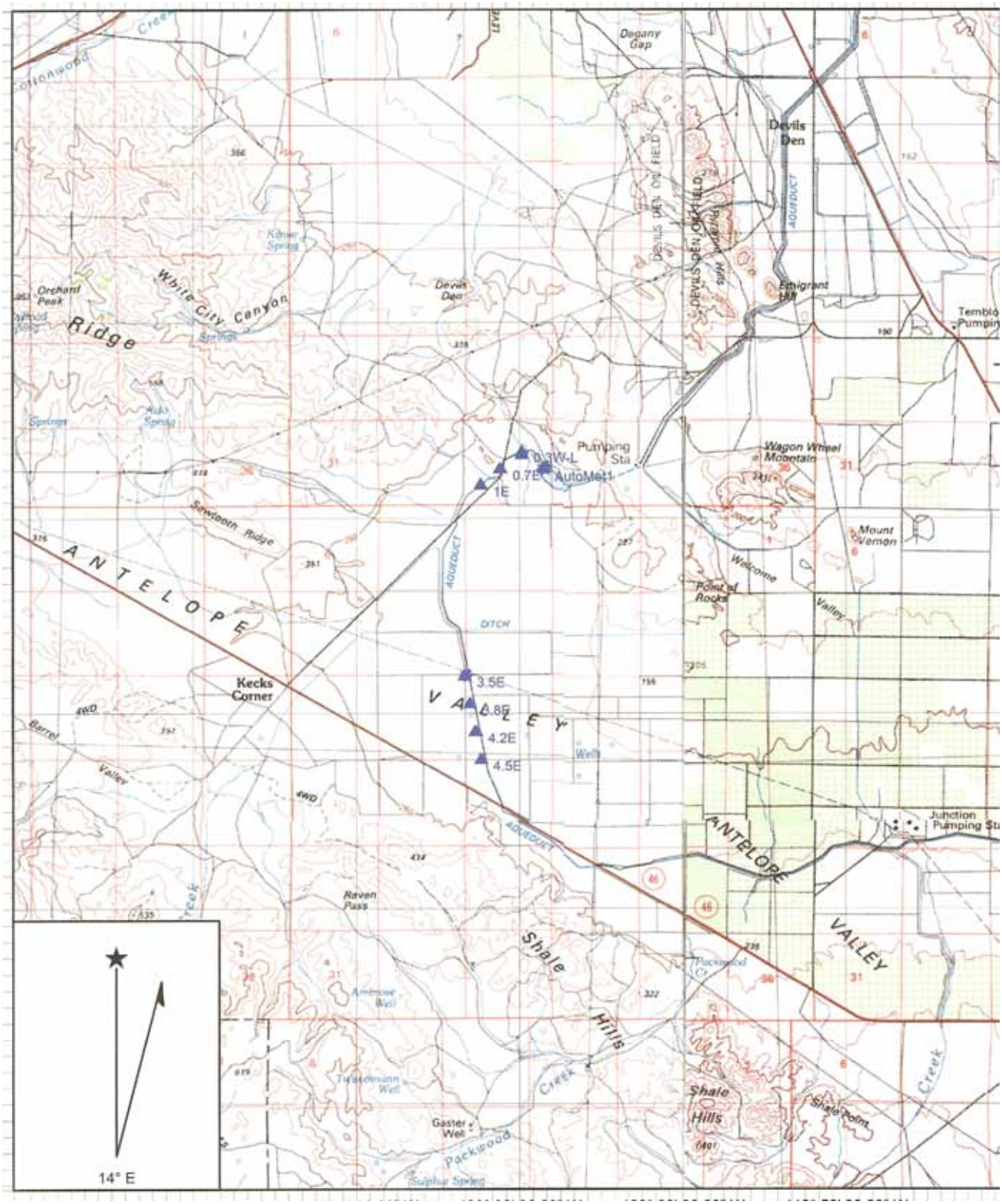

FIGURE 1: SAWTOOTH RIDGE TOPOGRAPHICAL OVERVIEW OF MONITORED AREA

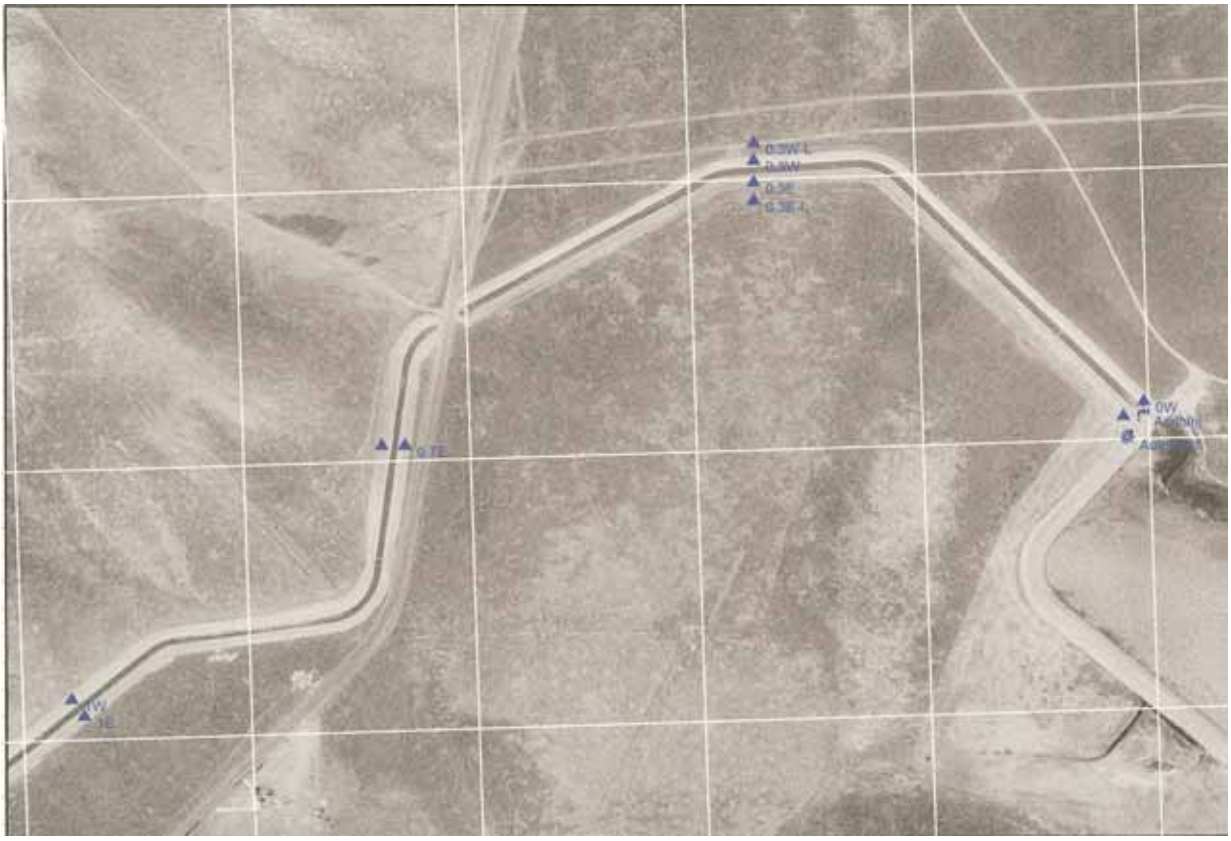

FIGURE 2: AERIAL PHOTO OVERVIEW OF 0-1 MILE SECTION

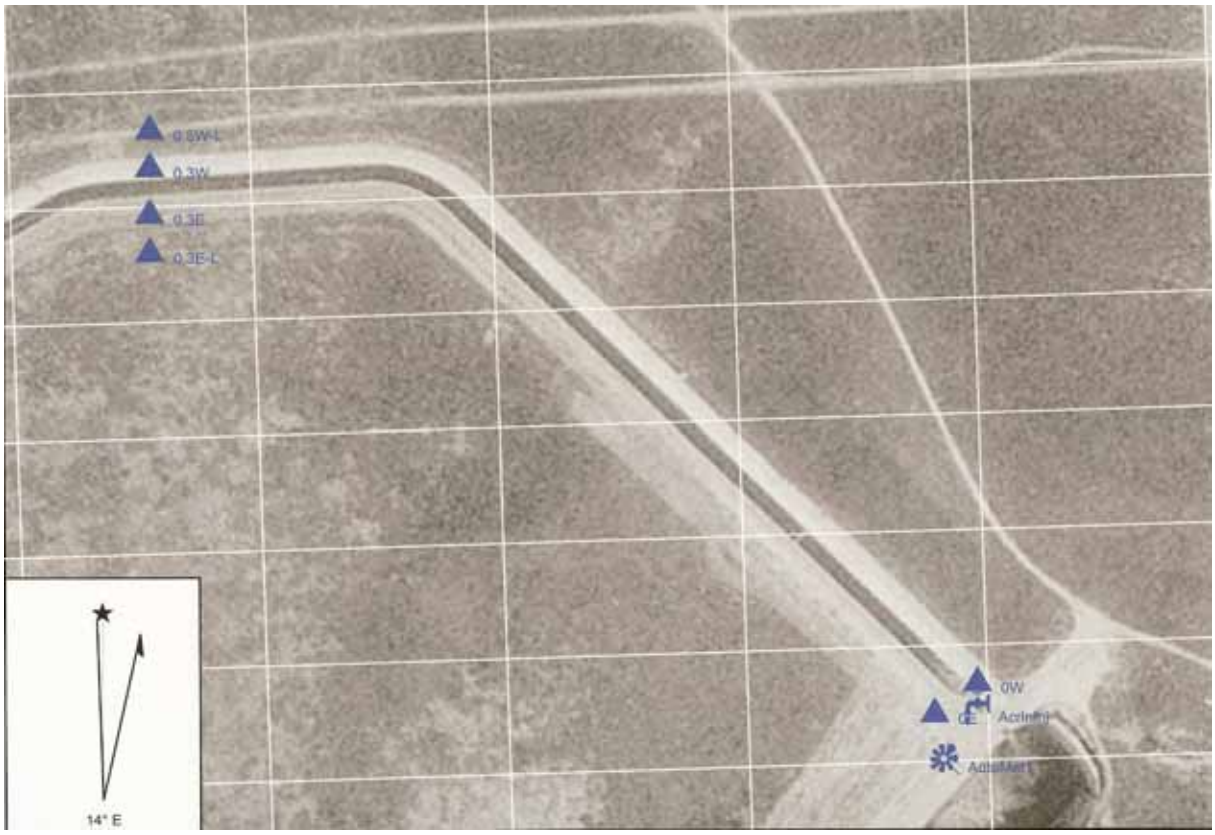

FIGURE 3: AERIAL PHOTO CLOSEUP OF 0 & 0.3 SITES

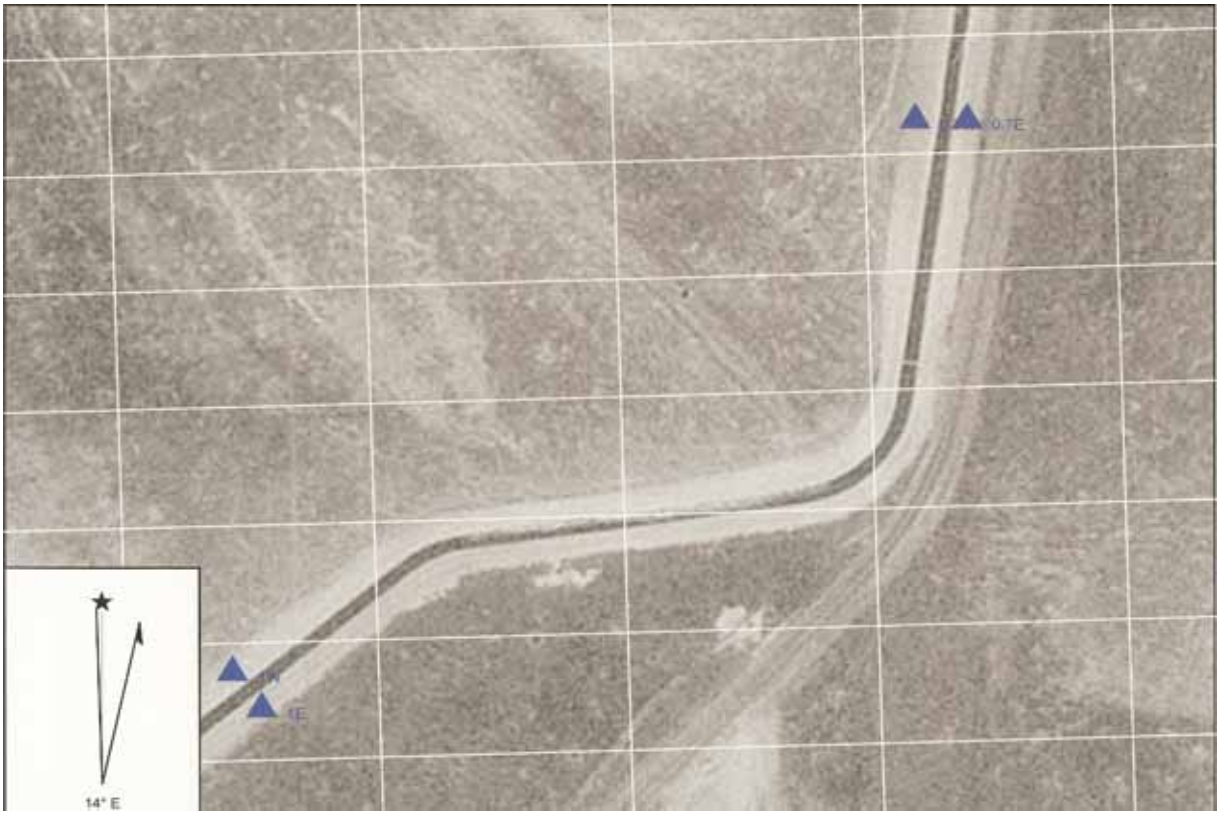

FIGURE 4: AERIAL PHOTO CLOSEUP OF 0.7 & 1 SITES

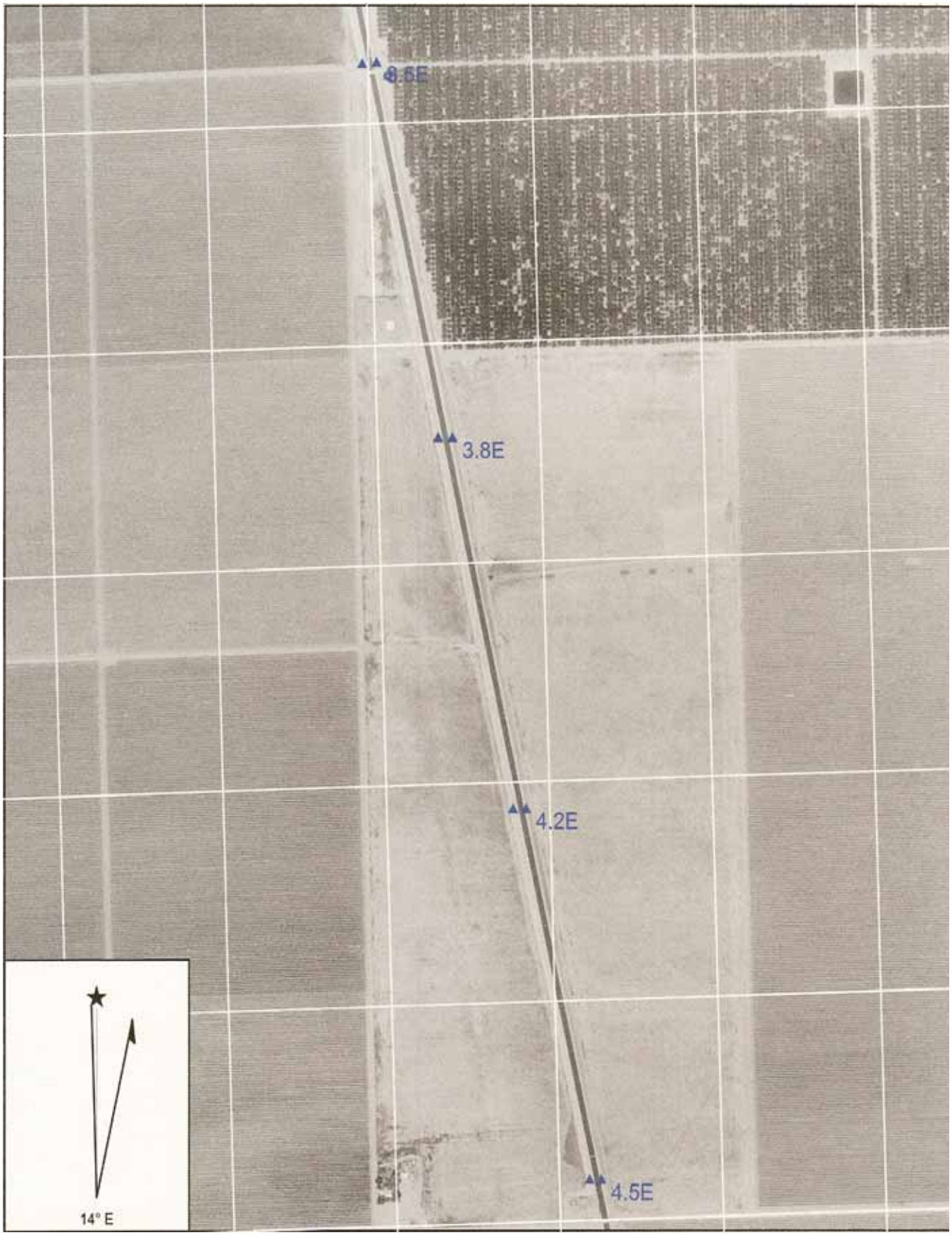

FIGURE 5: AERIAL PHOTO OVERVIEW OF 3.5-4.5 MILE SECTION

FIGURE 6: AERIAL PHOTO CLOSEUP OF 3.5 & 3.8 SITES

FIGURE 7: AERIAL PHOTO CLOSEUP OF 4.2 & 4.5 SITES

TABLE 1: APPLICATION INFORMATION

Parameter	Detail
Location	CA, Kern County, Lost Hills, Near 13406 Kecks Road
Range/Township/ Section	0-1 Mile Section = 18E/25S/33 & 3.5-4.5 Mile Section = 18E/26S/16W, Sawtooth Ridge 7.5' Topo
Canal Description	Generally 14' deep by 25' wide concrete lined. Water travelled at 1.48 mph with a discharge from the forebay gate of 189 cfs
Product Applied	Magnacide H Herbicide, 95.0% Acrolein plus 5.0% Inert Ingredients.
Application Type	Injection, Start = 0510, Stop = 0520, Restart = 0530 & End = 0830.
Commodity	Irrigation water
Application Rate	0.17 g/cfs, 189 cfs, 3 hrs., 31.5 gals. used, 10.5 gph, 1.8 ppm equivalent
Owner/Applicator	Berenda Mesa Water District/Staff

TABLE 2: APPLICATION SAMPLING PERIODS

Sampling Period	Sampling Duration (Hours)	Month & Year (July 2007)	Time (Start/Stop)
Background (Daytime)	4.08	24	11:21 to 15:26
0-1 Mile (Application)	4.28	25	05:30 to 09:55
3.5-4.5 Mile (Downstream)	4.35	25	07:45 to 12:15

TABLE 3: SAMPLER WAYPOINTS

Sampler ID	Sampler Position Related to Monitored Canal	Waypoints
AUTOMET1 (0-1 Sections Meteorology Station)	70' south of injection point along west side of dam, Elevation = 727'	N 35° 42' 29.99" W 120° 01' 40.87"
ACRLNINJ (Application Injection Point)	25' west of Forebay's gate to Berenda Mesa Canal, Elevation = 728'	N 35° 42' 30.85" W 120° 01' 40.21"
0E-C (0 Mile, East Side, Site With Collocated Sampler)	Alongside canal, 29' southwest of entry gate to canal, just after the injection pond, Elevation = 726'	N 35° 42' 30.84" W 120° 01' 41.04"
0W (0 Mile, West Side, Site)	Alongside canal, 29' northeast of entry gate to canal, just after the injection pond, Elevation = 730'	N 35° 42' 31.35" W 120° 01' 40.13"
0.3E (0.3 Mile, East Side, Site)	1,760 $\pm$ 5' downstream from 0E, 21' south of canal's water, Elevation = 725'	N 35° 42' 39.91" W 120° 01' 57.04"
0.3W (0.3 Mile, West Side, Site)	1,813 $\pm$ 5' downstream from 0W, 21' north of canal's water, Elevation = 727'	N 35° 42' 40.72" W 120° 01' 57.01"
0.3E-L (0.3 Mile Lateral, East Side, Site)	Alongside canal and perpendicular to 0.3E, 65' south, Elevation = 723'	N 35° 42' 39.25" W 120° 01' 57.06"
0.3W-L (0.3 Mile Lateral, West Side, Site)	Alongside canal and perpendicular to 0.3W, 65' north, Elevation = 728'	N 35° 42' 41.37" W 120° 01' 56.98"
0.7E (0.7 Mile, East Side, Site)	1,760 $\pm$ 5' downstream from 0.3E, 29' east of canal's water, Elevation = 731'	N 35° 42' 30.46" W 120° 02' 13.02"
0.7W (0.7 Mile, West Side, Site)	1,840' $\pm$ 5' downstream from 0.3W, 29' west of canal's water, Elevation = 734'	N 35° 42' 30.61" W 120° 02' 13.89"
1E (1 Mile, East Side, Site)	1,760' $\pm$ 5' downstream from 0.7E, 26' southeast of canal's water, Elevation = 728'	N 35° 42' 20.91" W 120° 02' 27.31"
1W (1 Mile, West Side, Site)	1,692' $\pm$ 5' downstream from 0.7W, 26' northwest of canal's water, Elevation = 730'	N 35° 42' 21.54" W 120° 02' 27.87"
AUTOMET2 (3.5-4.5 Sections Meteorology Station)	65' east of canal's water, 87' southeast of 3.5E site, Elevation = 725'	N 35° 40' 22.12" W 120° 02' 38.67"
3.5E (3.5 Mile, East Side, Site)	2.5 miles downstream from 1E, 18' east of canal's water, Elevation = 725'	N 35° 40' 22.74" W 120° 02' 39.40"

TABLE 3: SAMPLER WAYPOINTS (continued)

3.5W (3.5 Mile, West Sie, Site)	2.5 miles downstream from 1W, 18' west of canal's water, Elevation = 726'	N 35° 40' 22.75" W 120° 02' 40.25"
3.8E (3.8 Mile, East Side, Site)	1,760' ± 5' downstream from 3.5E, 23' east of canal's water, Elevation = 726'	N 35° 40' 05.71" W 120° 02' 35.35"
3.8W (3.8 Mile, West Side, Site)	1,753' ± 5' downstream from 3.5W, 23' west of canal's water, Elevation = 727'	N 35° 40' 05.74" W 120° 02' 36.18"
4.2E (4.2 Mile, East Side, Site)	1,760' ± 5' downstream from 3.8E, 23' east of canal's water, Elevation = 724'	N 35° 39' 48.70" W 120° 02' 31.36"
4.2W (4.2 Mile, West Side, Site)	1,751' ± 5' downstream from 3.8W, 23' west of canal's water, Elevation = 725'	N 35° 39' 48.72" W 120° 02' 32.14"
4.5E (4.5 Mile, East Side, Site)	1,760' ± 5' downstream from 4.2E, 18' east of canal's water, Elevation = 721'	N 35° 39' 31.73" W 120° 02' 27.33"
4.5W (4.5 Mile, West Side, Site)	1,750' ± 5' downstream from 4.2W, 18' west of canal's water, Elevation = 723'	N 35° 39' 31.73" W 120° 02' 28.07"

4.0 Methods

Background sampling was performed during the afternoon of July 24th. Background samples included two (2) samples and one (1) field spike. Eighteen samples plus two (2) collocated samples were collected on July 25th with an average hourly integrated air sample time of 4.24 hours. The air samples were collected by an air sampling assembly consisting of a 0.23 meter long by ¼" diameter Siltek treated stainless steel sample probe, passive Siltek treated stainless steel flow controller, and an evacuated 6 liter Summa canister. The inlets were placed at 67" ±2" above the ground. The sample flow rate was set to sixteen sccm as measured using calibrated transfer standard mass flow meters (MFM). Sample flow measurements were taken at the beginning and end of each sample collection period.

According to the sampling protocol, sampling was to begin 5-minutes prior to the beginning of the Acrolein application. However, ARB discovered that the application had started at 0510 hours. At ARB's request, the applicator stopped the application at 0520 hours. The application was restarted at 0530 hours along with the 0E and 0W samplers. For more detailed information refer to Section 2.0: Deviations From Protocol. The acrolein application was completed after three (3) hours at 0830 hours.

The sampling protocol stated that downstream samplers were to start upon the notification of the arrival of the Acrolein plume from samples obtained two hundred feet upstream from 3.5E. Baker Petrolite staff was not available to analyze samples for the plumes arrival. Thus, ARB staff started the first 3.5 – 4.5 mile section's samplers at 0745 hours based on the previously measured flow rate of the canal's water of 1.5 mph. For more detailed information refer to Section 2.0: Deviations From Protocol.

For details of the monitoring method, please refer to Appendix A, "Sampling Protocol for Acrolein Application Study" dated July 25, 2007. The canister sample start flows were set to approximately 16 sccm. For more detailed information refer to Section 2.0: Deviations From Protocol.

Upon completion of sample collection, canister samples were transported to the MLD laboratory in Sacramento by ARB staff. In addition to twenty ambient air samples, five quality control samples consisting of two collocated, a field spike, a trip spike, and a trip blank were also collected.

Collected samples were analyzed using the laboratory method, "Standard Operating Procedure For The Determination of Oxygenates and Nitriles In Ambient Air By Capillary Column Gas Chromatography/Mass Spectrometry", located in Appendix A as part of, "Sampling Protocol for Acrolein Application Study". No sample analyses exceeded concentrations above the calibration range, and therefore no additional dilution and re-analysis were required. Appendix C contains the laboratory results report entitled, "Acrolein Application Study Results" (September 2007).

5.0 Results

All collected samples and their respective analytical results are presented in Table 4: Acrolein Application Monitoring Results. These analytical results were obtained from Appendix C**,** **"**Laboratory Results Report". For additional information on the analytical results, please refer to Appendix C.

As mentioned in Section 3.0: Sampling Sites, the site nomenclature for this study was based upon the mileage point along the canal starting at the entry gate and ending at mile 4.5 downstream. Most of the canal generally ran north and south so each side was designated as east (E) or west (W). Additional letters were added, after inserting a dash to identify the type of sample collected (background, collocated or lateral).

Examples:

0E-B	=	Mile 0 East Site – Background
0E-C	=	Mile 0 East Site - Collocated
0.3W-L	=	Mile 0.3 West Site - Lateral
3.5W	=	Mile 3.5 West Site

Table 4: Acrolein Application Monitoring Results

Site	Log Number	Canister Number	Date Received	Date Analyzed	Results (ppb) Acrolein	Lab Certified Dilution Ratio	Lab Certified Arrival Vacuum, "Hg	Lab Certified Dilution Pressure, psig
0E-B	001E	80470	7/26/2007	7/30/2007	1.0	2.62	-10.0	11.0
0W-B	001W	80460	7/26/2007	7/30/2007	2.0	2.52	-10.0	10.0
0E	004E	80414	7/26/2007	8/2/2007	1.7	2.52	-10.0	10.0
0E-C	005E	89037	7/26/2007	8/2/2007	2.2	2.62	-10.0	11.0
0W	003W	67011	7/26/2007	7/30/2007	5.8	2.62	-10.0	11.0
0.3E	006E	3066	7/26/2007	8/2/2007	3.3	2.62	-10.0	11.0
0.3W	004W	3139	7/26/2007	7/30/2007	6.1	2.52	-10.0	10.0
0.3E-L	007E	67009	7/26/2007	8/2/2007	2.9	2.57	-10.0	10.5
0.3W-L	005W	80459	7/26/2007	7/30/2007	7.3	2.52	-10.0	10.0
0.7E	008E	80422	7/26/2007	8/2/2007	4.9	2.54	-10.0	10.2
0.7W	006W	73052	7/26/2007	7/30/2007	5.7	2.60	-9.8	11.0
1E	009E	9028	7/26/2007	8/2/2007	2.9	2.40	-9.0	10.0
1W	007W	76508	7/26/2007	7/30/2007	4.1	2.59	-9.5	11.2
3.5E	010E	65018	7/26/2007	8/6/2007	2.2	2.62	-10.0	11.0
3.5E-C	011E	73061	7/26/2007	8/6/2007	1.7	2.58	-10.0	10.6
3.5W	010W	67022	7/26/2007	8/2/2007	6.8	2.42	-9.0	10.2
3.8E	012E	80430	7/26/2007	8/6/2007	3.8	2.36	-8.5	10.1
3.8W	011W	73070	7/26/2007	8/2/2007	4.8	2.50	-9.0	11.0
4.2E	013E	80437	7/26/2007	8/6/2007	4.9	2.48	-9.0	10.8
4.2W	012W	89030	7/26/2007	8/6/2007	4.9	2.49	-10.0	9.7
4.5E	014E	80439	7/26/2007	8/6/2007	2.0	2.52	-10.0	10.0
4.5W	013W	76063	7/26/2007	8/6/2007	3.4	2.48	-9.0	10.8

Data completeness for this study was 100% of the twenty samples and five (5) quality control samples collected. The Field Spike was sampled for 3.1 hours due to a starting vacuum of -19"Hg. The normal starting canister vacuum is ≤-30"Hg. Sampling the field spike canister for any longer would have brought the vacuum to above -5"Hg which is too low a vacuum for the Restek flow controllers to reliably control the flow.

The laboratory's analytical results showed background levels of acrolein of 1.0 ppb for the 0W-B sample and 2.0 ppb for the 0E-B sample. Generally, the higher acrolein concentration results correlated with the wind directions recorded as the higher readings were recorded at sites downwind from the canal. See Appendix D for wind roses. The highest result of 7.3 ppb was recorded at 0.3W-L and the third highest result was 6.1 ppb recorded at 0.3W during the application sampling period in section 0 - 1 where the winds were from the south southeast. The second highest result of 6.8 ppb was recorded at 3.5W during the downstream sampling period in section 3.5 - 4.5 where the winds were from the east. Please note that diesel tractors, a source of acrolein emissions, passed by on the farm road located between sites 3.5E and 3.5W and the meteorological tower up to thirty five times during the sampling period.

Further reference material can be found in Appendix E which presents the field log sheets and Appendix F which presents the calibration/certification reports.

6.0 Quality Control Results

Quality Control samples collected from the field consisted of two collocated canisters, one Field Spike canister, one Trip Spike canister and one Trip Blank canister. The Quality Control results are summarized below. For more detailed information see Table 5: Acrolein Application Quality Control Results below and Appendix C of this report.

Collocated sample results were 2.2 ppb for 0E-C and 1.7 for 3.5E-C, with a Relative Percent Difference (RPD) (a-b ÷ [(a+b) ÷ 2] x 100 = RPD) of +25.6% for the 0E-C sample and -25.6% for the 3.5E-C sample as reported in Appendix C: Laboratory Results Report. The field spike recovery was 102%, the trip spike recovery was 101% and the trip blank result was less than the Limit of Detection (LOD).

Table 5: Acrolein Application Quality Control Results

Log Number	Sample Identification	Canister Number	Date Received	Date Analyzed	Results			Lab Certified	
					Expected (ppb)	Actual (ppb)	Recovery (%)	Arrival Vacuum	Dilution Pressure
002E	Field Spike	80451	7/26/2007	7/30/2007	9.6	11.0	114.6	N.E.	14.2
003E	Trip Spike	80446	7/26/2007	7/30/2007	12.0	11.0	91.7	-19.0	10.0
002W	Trip Blank	73056	7/26/2007	7/30/2007	<0.3	<LOD	N.A.	-30.0	10.0
005E	0E-C	89037	7/26/2007	8/2/2007	N.A.	2.2	N.A.	-10.0	11.0
011E	3.5E-C	73061	7/26/2007	8/6/2007	N.A.	1.8	N.A.	-10.0	10.6

LOD = Limit of Detection, N.E. = No Entry