



State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

**Pesticide Air Monitoring for Acrolein  
In Kern County  
June 2006**

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February 28, 2007

This report has been reviewed by the staff of the California Air Resources Board (CARB) 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

## Monitoring Report Approval

**Report Title:** Pesticide Air Monitoring for Acrolein in Kern County – June 2006

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

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## **Executive Summary**

### **Report on Ambient Air Monitoring For Acrolein in Kern County during June 2006**

The California Department of Pesticide Regulation's (DPR) final report dated May 2005, "Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredients Acrolein", recommends that the Air Resources Board (ARB) conduct a comprehensive air monitoring study for acrolein during a waterway application.

Before proceeding with a complete study, ARB's Monitoring and Laboratory Division (MLD) performed a pilot study on the morning of August 3, 2005, at Kern Island irrigation canal in the Kern Delta Water District in Bakersfield, California, to determine the applicability of the proposed acrolein field test method. A total of six ambient air samples were collected during the application. The acrolein concentrations observed during this application ranged from 15.9 to 59.8 ppb of acrolein. Laboratory analyses confirmed the applicability of the proposed field test method for use in a full-scale study.

MLD conducted a complete scale study at Kern Island irrigation canal on June 22, 2006. The field test method included a 4-hour background sample 18-24 hours before the application, a 4-hour sample period during the application a 4-hour post application sample period. The 4-hour application sample period was conducted during the day and started minutes prior to the injection of acrolein into the water canal for safety reasons. The 4-hour post application sample period was conducted at the end of the 4-hour application sample period. There were a total of 35 sample canisters (16 application, 14 post application, 2 background, 1 field spike, 1 trip spike, and 1 trip blank).

- Reported results for the 4-hour background with 2 valid samples indicated background concentrations of acrolein to be 1.1 and <1.5 ppb
- Reported results for the 4-hour application with 16 validated samples indicated ambient acrolein concentrations ranging from 8.4 to 24 ppb.
- Reported results for the 4-hour post application with 14 validated samples indicated ambient acrolein concentrations ranging from 1.2 to 5.3 ppb.

Quality control field samples included 2 collocated samples, 1 field spike, 1 trip spike, and 1 trip blank. The percent difference for the collocated acrolein samples were 8%. The background field spike recovery percentage for acrolein was 86%. The trip spike recovery percentage for acrolein was 101%.

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## 1.0 INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) (December, 2005 Memorandum; Warmerdam to Witherspoon), the Air Resources Board (ARB) conducted ambient air monitoring for the pesticide acrolein.

The recommended timeframe for acrolein monitoring, August to September, coincided with the hot weather and the growth of algae within the Kern Island Canal. The ARB had previously conducted a pilot ambient air monitoring study for acrolein August 3, 2005 at this same location. The results of the 2005 acrolein pilot study ranged from 15.9 to 59.8 ppb of acrolein. Following the 2005 acrolein pilot study, the ARB along with the DPR developed a more in-depth application monitoring study for the 2006 season. This 2006 acrolein study included samplers on each side of the canal near the acrolein injection point and down the accessible length of the canal. Two additional samplers were located further away from each side of the canal. The 2006 acrolein sampling and analysis procedures are outlined in the "Sampling Protocol for Acrolein Application Study" dated June 15, 2006 in (Appendix A).

Thirty three (33) canister samples were collected at fourteen (14) different monitoring sites in Kern County June 22, 2006. 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.

## 2.0 PERSONNEL

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### 3.0 SAMPLING SITES

The acrolein application had seven sampling sites on both the east and west sides of the irrigation canal. Six pairs of sampling sites were placed along the canal's dirt edge. One pair of lateral sampling sites was placed away from the side of the canal, between sites one and three on the west and east side of the canal. The two sites closest to the acrolein injection point were collocated during the 1<sup>st</sup> 4-hour sampling period.

The post application site locations were the same as the application configuration listed above except there were no collocated canisters.

The injection point for the acrolein was on the water intake side of the three culvert pipes located on the north side of a dirt road which crosses the canal. The first pair of air sampling sites was on the south side of the road and located on the west and east sides of the canal directly across from the water discharge side of three culvert pipes (see figure 1). The air samplers along the canal's dirt edge were as close as possible from the water's edge. The six ambient sampling sites on the west side of the canal's dirt edge were 50 meters apart in the downstream direction and the lateral sites were between site one and three at 25 meters, and ~10 meters from the canal's dirt edge. Due to the curvature in the canal, the west side sampling sites were used as a reference, to locate the seven samplers on the east side of the canal directly across from the west side ambient air samplers. The six east side samplers were placed along the canal's dirt edge as close as possible from the water's edge and the lateral site was located across from the west side lateral sampler at ~10 meters away from the canal's dirt edge. All sampler intakes were 1.7 meters (67 inches) above the ground.

Background sampling was conducted the day before the application on June 21, 2006, 18-24 hours prior to the application and sampled for approximately 4-hours. The background samplers were located at Site-1W and Site-1E (see figure 1), and one field spike was collocated next to Site-1E, (spiked with 54.7 ppb of acrolein). Due to the increased pressure in the spiked canister, both canisters at Site-1E were sampled until the field spike approached -5 inches of mercury. The canister at Site-1W sampled for approximately 4-hours. The background sites were located directly across from the discharge side of the three culvert pipes.



AERIAL PHOTO OF KERN ISLAND CANAL SAMPLING SITES

FIGURE 1

Sampler Site Names	Sampler location and distance from culvert pipe and sampling sites 1W and 1E	GPS Coordinates
1W, 1WC, 1WP, 1W-BKGD	West side of canal even with culvert discharge	N 35°23.986 W119°00.462
1E, 1EC, 1EP, 1E-BKGD, 1E-FS	East side of canal even with culvert discharge	N 35°23.981 W119°00.442
2WL and 2WLP	25 meters from 1W and 9.6 meters from canal	N 35°23.971 W119°00.466
2EL and 2ELP	19.5 meters from 1E and 10 meters from canal	N 35°23.971 W119°00.439
3W and 3WP	50 meters from 1W and by canals edge	N 35°23.958 W119°00.462
3E and 3EP	41.8 meters from 1E and by canals edge	N 35°23.959 W119°00.444
4W and 4WP	100 meters from 1W and by canals edge	N 35°23.931 W119°00.453
4E and 4EP	87.8 meters from 1E and by canals edge	N 35°23.939 W119°00.440
5W and 5WP	150 meters from 1W and by canals edge	N 35°23.907 W119°00.444
5E and 5EP	136.9 meters from 1E and by canals edge	N 35°23.908 W119°00.432
6W and 6WP	200 meters from 1W and by canals edge	N 35°23.879 W119°00.431
6E and 6EP	186.6 meters from 1E and by canals edge	N 35°23.855 W119°00.421
7W and 7WP	250 meters from 1W and by canals edge	N 35°23.855 W119°00.421
7E and 7EP	237.2 meters from 1E and by canals edge	N 35°23.859 W119°00.406
AUTOMET	50 meters from 1E and 10 meters from 3E	N 35°23.961 W119°00.438
WEIR FENCE TO 1W	13 meters (acrolein injection point)	N 35°23.986 W119°00.462
WEIR FENCE TO 1E	13 meters (acrolein injection point)	N 35°23.981 W119°00.442

W = West Side                      E = East Side                      FS = Field Spike  
 WC = West Collocated Sample    EC = East Collocated Sample    TS = Trip Spike  
 WP = West Post                      EP = East Post                      TB = Trip Blank  
 WL = West Lateral Sample        EL = East Lateral Sample        BKGD = Background

## SITE LOCATIONS AND GPS COORDINATES

**TABLE 1**

## **4.0 METHODOLOGY**

The sampling methodology utilized evacuated silco-steel, 6 litre canisters, passively filled with Restek critical orifice samplers.

For a complete description of sampling methodology, see Appendix A, Sampling Protocol for Acrolein Application.

The Organics Laboratory Section of MLD's Northern Laboratory Branch performed the analyses for acrolein collected by the canister method. This analytical procedure is entitled, "Standard Operating Procedure for the Determination of Oxygenates and Nitriles in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry" and may be found in its entirety at: [http://www.arb.ca.gov/aaqm/sop/sop\\_066.pdf](http://www.arb.ca.gov/aaqm/sop/sop_066.pdf)

## **5.0 RESULTS**

Sample data capture was 100%. One (1) minute average meteorological data was recorded for the background and application periods on June 21 and 22, 2006. This meteorological data is located in Appendix E along with the corresponding wind roses for each day. Table 2 below is the analytical data results from the laboratory. The indicated background concentrations of acrolein were 1.1 and <1.5 ppb. The application acrolein concentrations ranged from 8.4 to 24 ppb and the post application concentrations ranged from 1.2 to 5.3 ppb see figures 2 and 3 and Appendix D.

Sampling Location	Starting Time	Ending Time	Sampling Date	Receipt Date	Analysis Date	Acrolein Concent. (ppb)	Detection Limit (ppb)	Dilution Factor
TRIP BLANK	N/A	N/A	6/21/2006	6/26/2006	7/10/2006	<0.3	0.3	1
TRIP SPIKE	N/A	N/A	6/21/2006	6/26/2006	7/13/2006	10	0.9	3
1W-BKGD	7:30	12:30	6/21/2006	6/26/2006	7/10/2006	1.1	0.7	2.3
1E-BKGD	7:32	9:50	6/21/2006	6/26/2006	6/28/2006	<1.5	1.5	5.1
1E-FS	7:32	9:50	6/21/2006	6/26/2006	7/13/2006	11	0.9	3
1E	7:25	11:29	6/22/2006	6/26/2006	7/3/2006	15	2.3	7.7
1EC	7:25	11:29	6/22/2006	6/26/2006	7/3/2006	10	2.5	8.2
1EP	11:54	15:47	6/22/2006	6/26/2006	7/13/2006	3.2	0.8	2.6
1W	7:25	11:28	6/22/2006	6/26/2006	7/10/2006	11	2.3	7.8
1WC	7:25	11:28	6/22/2006	6/26/2006	7/3/2006	10	2.1	6.9
1WP	11:53	3:50	6/22/2006	6/26/2006	7/11/2006	5.3	0.8	2.6
2EL	7:26	11:15	6/22/2006	6/26/2006	7/13/2006	9.5	2	6.8
2ELP	11:58	15:49	6/22/2006	6/26/2006	7/11/2006	2.2	0.8	2.6
2WL	7:26	11:30	6/22/2006	6/26/2006	7/10/2006	10	0.7	2.4
2WLP	11:57	3:51	6/22/2006	6/26/2006	7/11/2006	1.4	0.7	2.4
3E	7:26	11:31	6/22/2006	6/26/2006	7/3/2006	14	2	6.6
3EP	12:01	15:51	6/22/2006	6/26/2006	6/28/2006	2.7	0.8	2.5
3W	7:26	11:30	6/22/2006	6/26/2006	7/3/2006	8.4	2.2	7.2
3WP	12:00	3:52	6/22/2006	6/26/2006	7/11/2006	2.7	0.8	2.6
4E	7:28	11:32	6/22/2006	6/26/2006	7/13/2006	20	1.6	5.2
4EP	12:06	15:53	6/22/2006	6/26/2006	7/10/2006	2.2	0.7	2.4
4W	7:27	11:32	6/22/2006	6/26/2006	7/13/2006	17	1.4	4.8
4WP	12:05	3:53	6/22/2006	6/26/2006	7/10/2006	1.9	0.8	2.5
5E	7:29	11:33	6/22/2006	6/26/2006	7/3/2006	13	2.1	6.9
5EP	12:09	15:55	6/22/2006	6/26/2006	7/10/2006	3.2	0.8	2.5
5W	7:28	11:32	6/22/2006	6/26/2006	7/13/2006	16	1.5	4.9
5WP	12:08	3:55	6/22/2006	6/26/2006	7/11/2006	2.6	0.8	2.5
6E	7:30	11:34	6/22/2006	6/26/2006	7/13/2006	18	1.6	5.3
6EP	12:12	15:58	6/22/2006	6/26/2006	7/3/2006	1.4	0.8	2.5
6W	7:29	11:33	6/22/2006	6/26/2006	7/13/2006	13	1.6	5.2
6WP	12:12	3:57	6/22/2006	6/26/2006	7/10/2003	1.2	0.7	2.4
7E	7:31	11:35	6/22/2006	6/26/2006	7/3/2006	11	2.1	7.1
7EP	12:16	16:00	6/22/2006	6/26/2006	7/10/2003	1.7	0.8	2.5
7W	7:30	11:34	6/22/2006	6/26/2006	7/13/2006	24	2.1	6.9
7WP	12:16	3:59	6/22/2006	6/26/2006	7/10/2003	2.4	0.7	2.4

## ACROLEIN RESULT

**Table 2**

Sampling Location	LAB Starting ("Hg)	FIELD Starting ("Hg)	LAB Ending ("Hg)	FIELD Ending ("Hg)
TRIP BLANK	-30	-30	-29.9	-30
TRIP SPIKE	-22	-22	-22	-22
1W-BKGD	-30	-30	-9	-8
1E-BKGD	<-30	-30	-21	-21
1E-FS	-22	-22	-10	-7.5
1E	-30	-29	-10	-7.5
1EC	-30	-29	-12	-11
1EP	-30	-30	-10	-9.5
1W	-30	-30	-12	-9
1WC	<-30	-30	-10	-7
1WP	-30	-30	-10	-9
2EL	-30	-29	-8	-6
2ELP	-30	-24	-11	-6
2WL	-30	-30	-8	-6
2WLP	-30	-30	-10	-8
3E	-30	-28	-8	-6
3EP	-30	-27.5	-11	-7
3W	-30	-30	-12	-6
3WP	-30	-29	-12	-9
4E	-30	-29	-10	-7
4EP	-30	-29	-10	-7
4W	-30	-28	-9	-7
4WP	-30	-30	-9	-7
5E	-30	-28	-7	-6
5EP	<-30	-30	-11	-9
5W	<-30	-30	-9	-7
5WP	<-30	-30	-8	-6
6E	<-30	-29	-11	-7.5
6EP	-30	-30	-9	-8
6W	<-30	-30	-12	-9
6WP	<-30	-30	-9	-8
7E	<-30	-29.5	-9.5	-6
7EP	<-30	-30	-10	-9
7W	<-30	-29	-9	-9
7WP	<-30	-30	-9	-9

CANISTER STARTING AND ENDING PRESSURES

TABLE 3

## 6.0 Quality Control

Quality control procedures were observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST)-traceable transfer standards were used to calibrate meteorological sensors and measure sample flow rates.

The sample flow rate of the passive flow controllers were measured using mass flow meters having a current calibration certification and a range of 0-100 cubic centimeters per minute.

The meteorological sensors were calibrated and aligned following the procedures outlined in the standard operating procedures on the Air Monitoring Web Manual at the following link.

<http://www.arb.ca.gov/aqdas/amwmn.php?c=5&t=sop>

Each sample canister was assigned a field sample report that provides identification of site, can ID number, operator, and sample information as well as sample transfer information.

Each sample was analyzed within the 30 day hold time established by stability studies for acrolein.

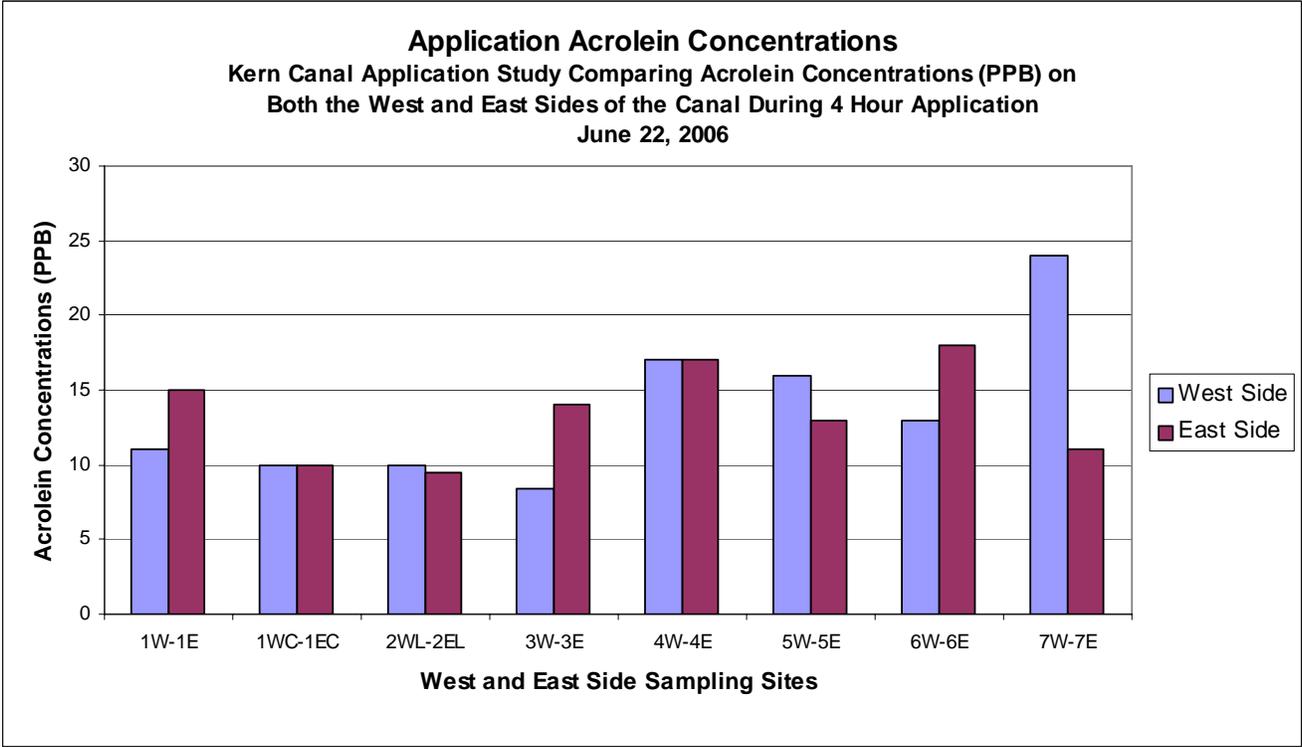
Collocated (side-by-side) air samplers were at two sites during the application period. These collocated sites were located at Site-1W and Site-1E.

A field spike canister was injected with a known quantity of acrolein by laboratory personnel. The field spike canister 1E-FS was collocated next to the background sampler 1E-BKGD. The field spike sampled for 2-hours and 18 minutes due to the starting canister pressure of -22 inches of mercury. The theoretical spiked concentration level was estimated at 10.7 ppb and the analysis value was 10.6 ppb minus the 1E-BKGD concentration of <1.5 ppb equaling 86 percent recovery (using 1.5 ppb 1E-FS value for the calculation).

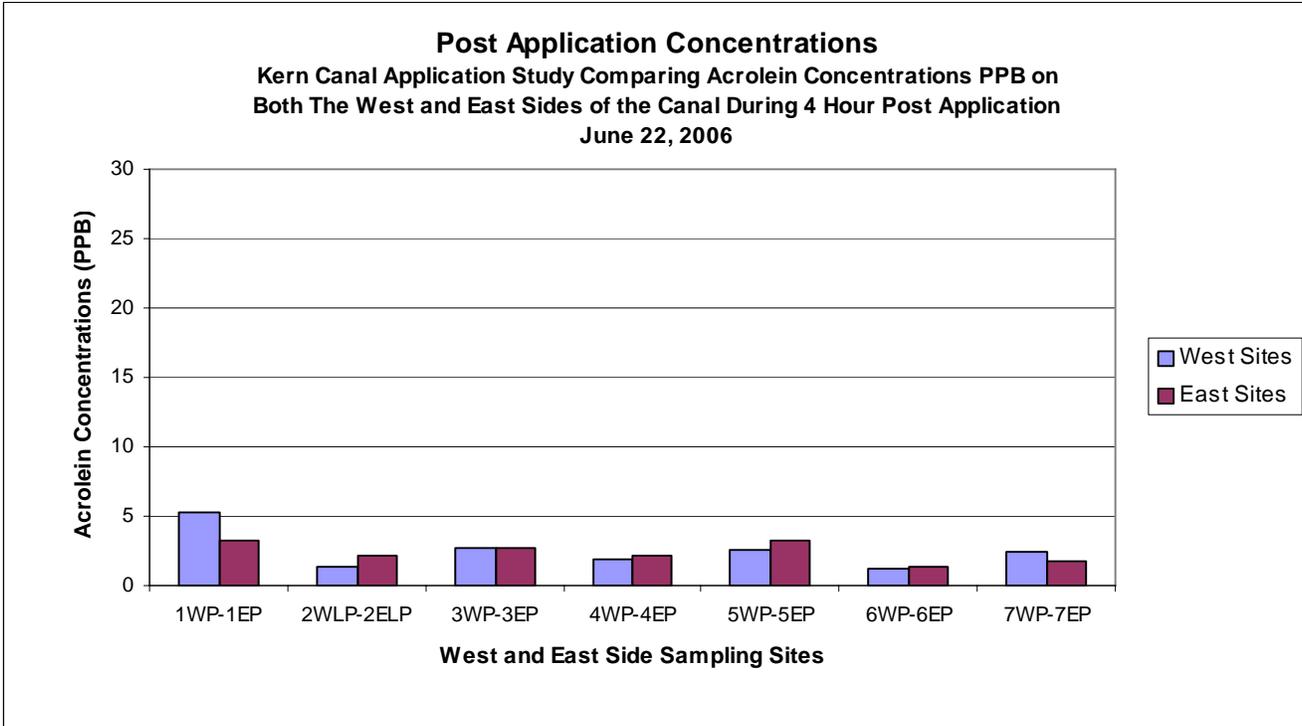
A trip spike was also injected with a known quantity of acrolein by laboratory personnel. The trip spike was transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler. The theoretical spiked concentration level was estimated at 10.3 ppb and the analysis value was 10.4 ppb which is 101 percent recovery.

The evacuated trip blank canister accompanies the sample canisters from the lab to the field and returned (not installed onto a sampler). The trip blank analytical concentration was <0.3 ppb.

The collocated samples Site-1WC and Site-1EC were located next to Site-1W and Site-1E and sampled during the same time frame of the application. Site-1W concentration was 11 ppb and Site-1WC was 10 ppb a percent difference of 9%. Site-1E concentration was 15 ppb and Site-1EC was 10 ppb a percent difference of 33%.



GRAPH OF APPLICATION RESULTS  
**Figure 2**



GRAPH OF POST APPLICATION RESULTS  
**Figure 3**