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SUBJECT: AIR DISPERSION MODELING ANALYSIS OF PRIORITY INCIDENT 38-MON-05

I. Background

On the evening of October 5, 2005 residents of the Salinas neighborhood of Creekbridge experienced irritant symptoms consistent with exposure to chloropicrin, including burning eyes, throat irritation, and nausea (Sowersby, 2005). According to the Priority Incident Report (Sowersby, 2005, Tab 19) and an October 6, 2005 article in The Salinas Californian (Calderon, 2005), emergency responders also experienced irritant symptoms, particularly including burning eyes. The suspected source of the irritant is a strawberry field that had been fumigated earlier in the day with chloropicrin by drip method.

This memorandum presents analysis of the chloropicrin application relative to the episode in order to assist in the assessment of the likelihood that this application could have been the source of the irritant that caused the episode. Estimates of chloropicrin air concentrations on the evening of October 5, 2005 are included.

II. Timeline

A. Application and Follow-up Sprinklers (times are approximate)

Drip Application: 1100hrs – 1700hrs

Drip Line Flushing: 1700hrs – 1745hrs

Sprinkler Watering-in:
Sprinklers 1800hrs – 2100hrs
Boosters 1900hrs – 2100hrs

Interviews in the Priority Incident Report **(**Sowersby, 2005) support the timeline shown above:

Page 1. The Summary states that sprinklers were turned on at approximately 1930hrs.
Page 3. October 6, 2005. Hank Guerrero stated that the sprinklers were turned on at approximately 1920hrs.
Page 5. October 10, 2005. Circo Sanchez does not specifically state when he turned on the sprinklers but stated that the booster pump was turned on at approximately 1930hrs. He also stated that the boosters ran until 2100hrs.
Page 6. October 10, 2005. Roberto Lincona stated: "After the injection was complete we flushed the lines for 45 minutes. Ciro and Abraham then opened up the valves to get ready to put the water cap on. About 10 minutes to 6 p.m., I went over to Block 20 and monitored the sprinklers with Ciro and Abraham to check for any blow outs…The sprinklers ran for about an hour and we monitored the field the whole time. I did smell the chloropicrin and experienced some burning in my eyes but it was the same with the two previous applications…Sometime after 8:30 p.m. we shut off both pumps…"
Page 11. October 14, 2005. Roberto Lincona stated: "At about 5:30 p.m., Circo opened the valve, right next to the fields, to turn on the sprinklers. I smelled the pic after the sprinklers had been turned on, but before the boosters had been fired up." Thus, he indicated that the sprinklers were turned on at 1730hrs and the boosters turned on at 1830hrs. He stated: "When Ciro hit the booster I didn't smell any pic, it was only when the sprinklers were first fired up." He stated that the sprinklers ran until about 2030hrs.
Page 13. October 14, 2005. Ciro Sanchez stated: "…I began calculating the 45 minute flush time, which ran until a quarter to six or so. When the flush time was over Abraham and I … opened the valve to the sprinkler. When I opened the 6 inch valve to the sprinklers I felt the pic a little… I thought there may have been some pic trapped in the riser… I turned on the booster at about 7 p.m. …When I initially fired up the booster the smell went away… I turned off the booster a little before 9 p.m."

When all the interviews are taken together the following conclusions seem clear: (1) the accounts on pages 1, 3, and 5 are referring to turning on the boosters and (2) the sprinklers were turned on immediately following the flush time. Thus, the sprinklers were first turned on at approximately 1800hrs followed by the boosters at approximately 1900hrs. The "flush" of chloropicrin from the sprinklers would have occurred at approximately 1800hrs. The Dye Test results (Sowersby, 2005, Tab 34) indicate that when the sprinklers were turned on chloropicrin laden water likely flowed from sprinklers at the most for 2 minutes.

B. Selected 911 Emergency Calls

The 911 call log (Sowersby, 2005, Tab 30) is used to establish the incident timeline since this is the most accurate and well documented timeline.

2014hrs – First call, New Hampshire Ct. (~ 0.5mi)

2052hrs – Farthest call, Las Casitas Dr. (~1.2mi)

2141hrs – Call indicating irritant is still present Ranchero Dr. (~1.0mi)

2158hrs – Officer on scene remarks "still pretty strong at Boronda/Constitution." (~0.5mi)

2208hrs – Last call reporting irritant symptoms, Constitution Blvd. (~0.5mi)

Neighborhood interviews after the incident suggest that some residences experienced irritant symptoms during the 1900hr–2000hr (Sowersby, 2005, Tab 28)

III. Estimated Chloropicrin Air Concentrations

A. Flux estimates

(1) The Initial Sprinkler Release

The sprinklers were used to apply water to the furrows with the purpose of suppressing chloropicrin loss from the exposed soil surface in the furrows. However, according to the investigation results, due to inadequate flushing time following the drip application, it is likely that chloropicrin was still in the water contained in the irrigation pipes when the sprinklers were turned on. This water would be a source of chloropicrin that could be lost to the atmosphere from a water/chloropicrin solution on the surface of the furrows and the tarps on the beds.

Estimates of the volume of the main sprinkler line together with the target concentration of the chloropicrin for the drip application can be used to estimate the mass of chloropicrin that, in effect, was applied directly onto the surface during the initial minutes of the sprinkler application. The largest diameter of the irrigation pipe is listed as 8 inches. The investigation states that the pipe diameter is reduced to 6 inches and then 4 inches as the main irrigation pipe extends from the injection point across the fields. The location of the pipe reductions is unknown. In addition, one diagram indicates an 8 inch valve located close to Block 20. Therefore, as a conservative assumption, an 8 inch diameter pipe for the entire length between the injection point and Block 20 will be assumed. This assumption will result in a larger volume of water than was likely available in the main irrigation pipe.

The estimated length of the main irrigation pipe from the injection point to Block 20 is approximately 4370ft. The volume of the pipe is calculated as:

$$\pi r^2 l = ft^3 = \pi(0.33)^2(4370) = 1495\ ft^3 = 11{,}183\ gal$$

The mass of chloropicrin available to be released through the sprinklers from the main irrigation pipe is calculated based on the assumption that the all the water in the pipe is at the application rate concentration of 885ppm chloropicrin. This maximum mass of chloropicrin is calculated below:

lbs chloropicrin = gallons * 2.2lb/kg * 1 kg/1,000,000 mg * 3.785 liters/gal * 885ppm

$$\text{lbs chloropicrin} = 11183 * (8.327 * 10^{-6}) * 885ppm = 82.4\ lbs$$

Therefore, approximately 82 lbs of chloropicrin is the estimated maximum mass available to be released through the sprinkler heads and applied directly to the surface of the field (tarped beds and furrows). Dr. Husein Ajwa stated that his calculated required flush time of the drip system was 90 minutes (Sowersby (2005), page 16). The drip lines were flushed for only 45 minutes. A simplifying assumption is that the 45 minute flush time reduced the chloropicrin mass by approximately half. It will also be assumed that the mass of chloropicrin released from the sprinklers was released to the entire 12.1ac block. Based upon these calculations an "application rate" from the sprinklers can be calculated:

$41.2lbs/12.1ac = 3.4lb/ac = 0.382g/m^2$

This estimate does not include any chloropicrin that may have been in water in side-lines off the main sprinkler line. Since irrigation water continued to be applied to the field after the initial chloropicrin deposition, the chloropicrin solution was continually diluted and rinsed off the tarped surface of the beds. Some of the chloropicrin would also have percolate into the soil in the furrows.

The rate of volatilization of the chloropicrin that was applied to the surface through the sprinklers is unknown. However, some assumptions can be made to establish whether it is likely this incident was caused exclusively by the chloropicrin lost through the sprinklers. According to the 911 call log timeline: the first call was received at 2015hrs, the last call from persons experiencing symptoms was received at 2208hrs. In addition, at 2158hrs the officer on scene remarks "still pretty strong at Boronda/Constitution." The sprinkler release of chloropicrin occurred at approximately 1800hrs. Therefore, to be exclusively from the sprinkler source, the volatilization must have occurred over a minimum of 3 1/2 hours. For calculation purposes

4 hours will be used and it will be assumed that 100% of the sprinkler source chloropicrin was volatilized over that 4 hours. The 4-hr time weighted average (TWA) flux is shown below:

$(0.382 g/m^2)/14400 sec = 26.5 ug/m^2 sec$

This flux estimate assumes: (1) the mass of chloropicrin is uniformly deposited on the surface of the entire field and (2) the irrigation water diluting the chloropicrin mass initially deposited did not slow the flux over time. Wofford (2005) estimated for a sprinkler application of metam sodium that approximately 50% of the applied mass of methyl isothiocyanate (MITC) was lost during the 6 hour application period. Based upon these results for the loss of MITC following sprinkler application of metam sodium it seems unlikely that all of the chloropicrin mass deposited by the sprinklers to this field was lost in 4 hours. However, since the Henry's Law Constant for chloropicrin is an order of magnitude larger than for MITC it is possible that the majority of the any sprinkler deposited chloropicrin left on the surface of the field volatilized from the surface of the field over 6 hours. Therefore, the 4 hour volatilization assumption can be argued as conservative.

(2) Chloropicrin Volatilization Following the Application

Chloropicrin loss from volatilization of mass applied during the drip application is in addition to any chloropicrin volatilization from mass accidentally released through the sprinklers. There is always loss of a fumigant following an application. Application methods differ in the pattern of loss. However, patterns for different fumigants using the same application method are often quite similar.

For the drip application method, a pattern of highest air concentrations and flux occurring in a 4–6 hour period following completion of the application (including flush time) is consistent across fumigants (e.g. chloropicrin, iodomethane, and metam sodium). This peak in air concentrations and flux in the 4–6 hours following application also appears to be consistent whether the application is completed early in the day or near nightfall. Rotonardo (2004) estimated that 6% of the applied chloropicrin mass was lost in the peak 4 hour sampling interval following the application. Although the Rotonardo (2004) sampling interval was during the day, the flux profile pattern is consistent with both day and night drip applications of iodomethane. Therefore, it will be assumed that 6% of the 200lb/ac was lost over the first 4 hours after the application was completed. For this incident the 4 hour period following the application would be from approximately 1830hrs to 2230hrs. Calculations for the flux estimate are shown below:

Application rate = $200 lb/ac = 22.4 g/m^2$

$((22.4 g/m^2) * 0.06)/14400 sec = 9.34 \times 10^{-5} g/m^2 sec = 93.4 ug/m^2 sec$

B. ISC modeling

Air dispersion modeling was used to produce air concentration isopleths for the hours of the incident. The U.S. Environmental Protection Agency (EPA) model Industrial Source Complex 3 (ISC3) was used for the simulations (U.S. EPA, 1995). This is a Gaussian Plume air dispersion model. The geometry of Block 20 was used together with a "unitized flux" of 100 ug/m^2sec and weather data from the California Irrigation Management System (CIMIS) station 116 (Monterey Bay–Salinas North) to produce generic plume isopleths for each hour. These generic plume isopleths are independent of the cause of the flux (e.g., sprinkler release versus the application itself) and thus, can be used to assess whether it is likely a plume of chloropicrin traveling off-site would have contacted the residential areas where the 911 calls originated. In the ISC3 model, air concentrations are directly proportional to the flux. Therefore, the unitized flux concentrations can be easily adjusted according to the flux values calculated above. Uncertainty in the flux estimates can be accounted for in these adjustments. However, it is most important first to assess whether the plume traveled in the direction of the residences.

Block 20 is the section farthest to the north and east of the agricultural parcel that is partitioned into 20 separate sections (Figure 1). Although throughout the investigation report Block 20 is referred to as 13 acres in size, the diagram showing the blocks labels Block 20 as 12.1 acres. Confirmation that Block 20 was the 12.1 acre treated site was received from Karen Stahlman of the Department Pesticide Regulation's (DPR's) Enforcement Branch (per. comm.). Block 20 was modeled as a polygon. Universal Transverse Mercator (UTM) coordinates around the perimeter of the block were obtained from ArcView software (ESRI, Inc.). Weather data used in the modeling is shown in Table 1. The generic input file used for modeling is available in Appendix A.

Concentration isopleths for each of the hours between 1900hrs and 2200hrs were produced using Surfer7 software (Golden Software, 1999). Locations of key residences that called 911 during the incident are shown as colored dots on Figures 2 through 13. There were no calls received during 1900hrs–2000hrs, however, for location reference the first call received is shown as a red dot in Figures 2, 5, 8, and 11. In addition, the locations of the residences that indicated in later interviews that they experienced irritant symptoms during the 1900hr–2000hr are shown as yellow dots in Figures 2, 5, 8, and 11. For the 2000hr–2100hr interval, the location of the calls are shown as yellow dots in Figures 3, 6, 9, and 12. For the 2100hr–2200hr interval the location of a calls during the hour and the last call received just after 2200hrs are shown as yellow dots, and the location of a police officer's report is shown as a red dot in Figures 4, 7, 10, and 13.

For the unitized flux analysis estimates of uncertainty in the location of the plume centerline during each hour were calculated according to the method of Sajo (2003). Figures 2 through 4 show the centerline plume location and the uncertainty bounds as red lines. The uncertainty bounds (outer most lines) shown are the approximately 80% confidence bounds on the location

of the plume centerline during the hour. This method has been previously employed to provide centerline location uncertainty estimate (Barry, 2005). See Appendix B for a complete presentation of the uncertainty estimation.

IV. Mapping Methods

The figures were prepared using ArcGIS® ArcMap Version 9.1 software (ESRI Inc., 2005), ArcView GIS 3.2 (ESRI Inc., 2000), and Surfer® (Golden Software, Inc., 1999).

Data layers included:

A digital ortho-imagery data set of Monterey County (2005) was obtained from the USDA-FSA Aerial Photography Field Office. The imagery resolution is 1 meter with North American Datum (NAD) 1983 and was projected in UTM projection Zone 10. The extent of the imagery was defined and used as a backdrop for presenting the isopleths generated from the Surfer modeling analysis.

A layer file from Dynamap® (Geographic Data Technology, Inc., 2002) representing streets in Monterey County was projected into NAD 83, UTM Zone 10. The street file was geocoded and used to query locations that had phone reports of the chloropicrin incident. A point layer was created from the query results to represent phone call locations.

A polygon shapefile was made (NAD83, UTM10) to represent the application site field boundary by outlining the field over the imagery using the ArcView polygon line tool. The NAD83 UTM Zone 10 coordinates of this field boundary were then used in the Surfer modeling program.

Surfer files were imported as shapefiles into the ArcGIS map project and projected at NAD83, UTM10 to overlay upon the imagery file. The tables were edited in ArcView to create a color legend of the isopleths representing concentrations. The median lines in the unitized figures were placed on the imagery by plotting a line from the center of the field and extending it through the center of the isopleths. The confidence boundaries were then plotted to represent the corresponding angle values calculated by the model.

V. Results

Note on wind direction. Wind direction is conventionally reported as the “from” direction. For example, southerly wind implies the wind is blowing from the south to the north (from 180°). However the convention in air dispersion modeling, and in this memorandum, is to report the wind direction, and the plume centerline direction, as the “to” direction. Thus a wind direction of 90° means the wind is blowing from the west to the east.

A. Unitized flux results

Figures 2 through 4 show the hourly mean location of the plume as characterized by the CIMIS weather data. These plumes are shown independent of the flux estimates and are provided to assess the likely direction of chloropicrin travel. Uncertainty estimates on the plume centerline location are also shown as red lines to either side of the mean plume centerline location. The uncertainty estimates are the approximately 80% confidence bound on the location of the plume centerline for each hour. See Appendix B for details on the calculation of the uncertainty estimates.

1900hrs–2000hrs. The previous hour (1800hrs–1900hrs) the mean wind direction was 83.5°. During 1900hrs–200hrs the mean wind direction shifted to the southwest (202.2°) (Figure 2). The plume did likely contact residences during this hour. However, the standard deviation of horizontal wind direction (sigma theta) was large, 64.2°. The large sigma theta indicates that the plume centerline location varied widely during this hour. This large sigma theta was likely the result of 2 factors: (1) the large shift in mean direction from the previous hour (83° to 202°), and (2) the drop in wind speed after sunset (1844hrs PDT). According to the CIMIS weather data, the mean centerline plume direction was 202.2°. With approximately 80% confidence, the centerline direction for the chloropicrin plume emitting from Block 20 during 1900hrs-2000hrs PDT on October 5, 2005 lies between approximately 140° and 265°.

2000hrs–2100hrs. The general direction of the unitized flux chloropicrin plume is shown in Figure 3. The plume is squarely located in the neighborhood where the calls were received. According to the CIMIS weather date, the mean centerline plume direction was 225.9°. Sigma theta is substantially smaller for this hour, 13.9°, indicating a persistent presence of the plume centerline in the same general direction for the entire hour. With approximately 80% confidence, the centerline direction for the chloropicrin plume emitting from Block 20 during 2000hrs–2100hrs PDT on October 5, 2005 lies between approximately 203°° and 249°.

2100hrs–2200hrs. The general direction of the unitized flux chloropicrin plume is shown in Figure 4. According to the CIMIS weather date, the mean centerline plume direction was 230.3°. With approximately 80% confidence, the mean centerline direction for the chloropicrin plume emitting from Block 20 during 2100hrs–2200hrs PDT on October 5, 2005 lies between approximately 198°° and 263°.

B. Concentration estimates

To evaluate whether it is likely people would be aware of the plume (e.g. concentrations are above the irritant threshold) the unitized isopleths can be adjusted according to the estimated flux for a particular averaging period.

Sprinkler source. Figures 5 through 7 show the estimated 1-hr TWA chloropicrin air concentration isopleths originating from the chloropicrin mass release through the sprinklers alone. The Estimated 1-hr TWA chloropicrin air concentrations in the areas where the 911 calls originated were below 0.10 ppm.

Application source. Estimated air concentrations are shown in Figures 8 through 10. This incident occurred in the hours just after the completion of the drip application process (including the flushing of the lines) coinciding with the period when the highest flux was observed in the Rotondardo (2004) chloropicrin drip method study. The completion of the drip application also coincided with sunset when the wind speed dropped, very stable atmospheric conditions developed, and the wind direction shifted directly toward the neighborhoods where the 911 phone calls originated. The Estimated 1-hr TWA chloropicrin air concentrations in the areas where the 911 calls originated range from 0.05ppm to 0.20ppm.

Composite source. The chloropicrin air concentration plume that residents were likely exposed to was a composite of the flux from the chloropicrin on the surface of the field and the flux from the application itself. Figures 11 through 13 show the isopleths of the composite plumes for each hour. The Estimated 1-hr TWA chloropicrin air concentrations in the areas where the 911 calls originated range from 0.05ppm to 0.20ppm.

V. Discussion

The unitized flux analysis indicates that during the hours of the incident it is reasonable to conclude that a plume originating from Block 20 would have contacted the neighborhoods where the 911 calls originated. It is unlikely that the initial release of chloropicrin when the sprinklers were first turned on at approximately 1800hrs caused the incident because the wind direction was away from the neighborhoods at that time. However, the mass of chloropicrin deposited out of the sprinklers directly onto the surface of the field was available to volatilize and move off-site later in the evening. Volatilization of this chloropicrin from the tarp and furrow surfaces was in addition to the usual volatilization loss expected following any chloropicrin application. The concentration isopleths indicate that it is likely the drip application itself was a significant contributor. Thus, the composite source of the sprinkler released mass and the usual volatilization expected following the application likely caused chloropicrin air concentrations sufficient to be detectable by some persons. In areas where calls originated during the incident estimated 1-hr TWA chloropicrin air concentrations were at or above 0.15ppm, the level causing eye irritation (ACGIH, 1992). In addition, peak to mean adjustments (Barry, 2000) (Table 2) produce shorter term estimated air concentrations in other areas that are also above 0.15ppm. These 1-hr TWA chloropicrin air concentration estimates are similar in magnitude to 1-hr TWA estimates for a previous chloropicrin incident where residents were similarly affected in 2003 in Kern County (Barry, 2003).

Although there were no 911 calls during 1900hrs–2000hrs, interviews after the fact indicate that there may have been households affected during 1900hrs–2000hrs. One possible explanation for the lack of calls prior to 2000hrs is the large standard deviation of horizontal wind direction for the 1900hr–2000hr. This large standard deviation associated with the mean wind direction indicates that the plume centerline location shifted frequently during the hour, potentially leading to brief effects in localized areas followed by relief due to change in plume direction. Essentially, during the 1900hr–2000hr period, it is likely the plume was not stationary in any one area. However, during the two hours of the incident, 2000hrs–2200hrs, the standard deviation of horizontal wind direction each hour was substantially smaller, indicating a relatively stationary plume location. That stationary plume behavior is reflected in the number of 911 calls.

An additional factor that cannot be accounted for with the ISC model is the relative elevation of the field compared to the neighborhood. Block 20 is located at an elevation of 36m (118ft) while areas where 911 calls originated are at an elevations ranging from 27m (90ft) to 18m (60ft). The neighborhoods involved in this incident are located in the Natividad Creek drainage. Due to night air drainage (Stull, 1988), this topographic feature may have lead to localized higher concentrations than the model predicted.

The uncertainty in chloropicrin flux estimates cannot be quantified. The flux of chloropicrin mass released by the sprinklers is most uncertain. However, no data on flux of chloropicrin from such a source exists. In addition, DPR has only one accepted study providing flux estimates for the chloropicrin drip application method. Other fumigants differ by approximately 20% in 8-hr flux estimates between studies for the drip method where the applications were completed close to sunset.

VI. Conclusion

Although there is uncertainty in the magnitude of chloropicrin air concentrations associated with the chloropicrin applied to Block 20, there is sufficient support to conclude that a plume of chloropicrin originating from Block 20 did contact the residences where the 911 calls originated during the 38-MON-05 incident.

V. References

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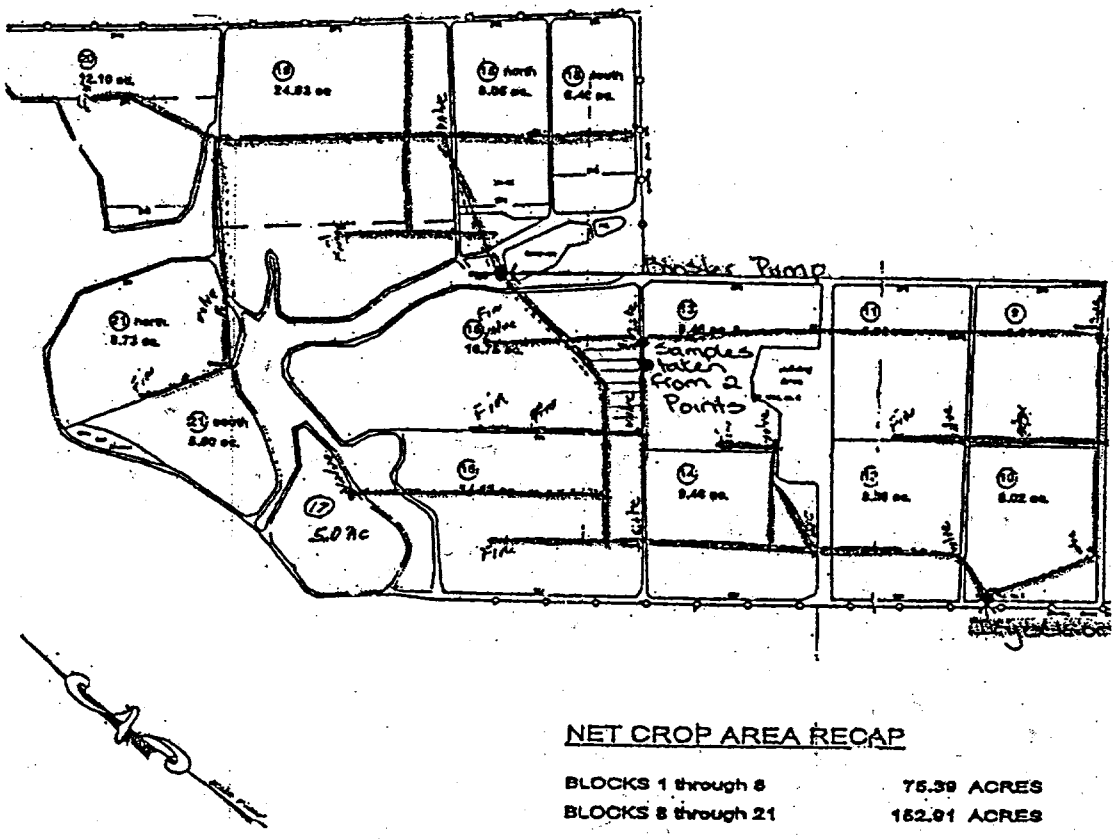
Table 1. Weather data from CIMIS Station 116–Monterey Bay–Salinas North.

Hour	Wind Speed (m/s)	"To" Wind Direction (degrees)	Wind Direction Std Dev (degrees)	Stability Class
1800–1900	1.16	83.5	17.9	E
1900–2000	0.98	202.2	64.2	F
2000–2100	1.47	225.9	13.9	F
2100–2200	1.16	230.3	21.2	F
2200–2300	1.03	299.0	36.7	F

Table 2. Estimated peak concentrations associated with 1-hr TWA chloropicrin air concentrations (ppm).

1-hr TWA Concentration (ppm)	30 minute TWA Concentration (ppm)	10 minute TWA Concentration (ppm)	3 minute TWA Concentration (ppm)
0.05	0.06	0.11	0.20
0.10	0.13	0.23	0.40
0.15	0.19	0.34	0.60
0.20	0.26	0.46	0.80

Figure 1. Diagram of individual blocks at Duncan Ranch/Daren's Berries Site. Priority Investigation 38-MON-05.



NET CROP AREA RECAP

BLOCKS 1 through 8	75.39 ACRES
BLOCKS 8 through 21	152.91 ACRES
TOTAL NET CROP AREA	228.30 ACRES